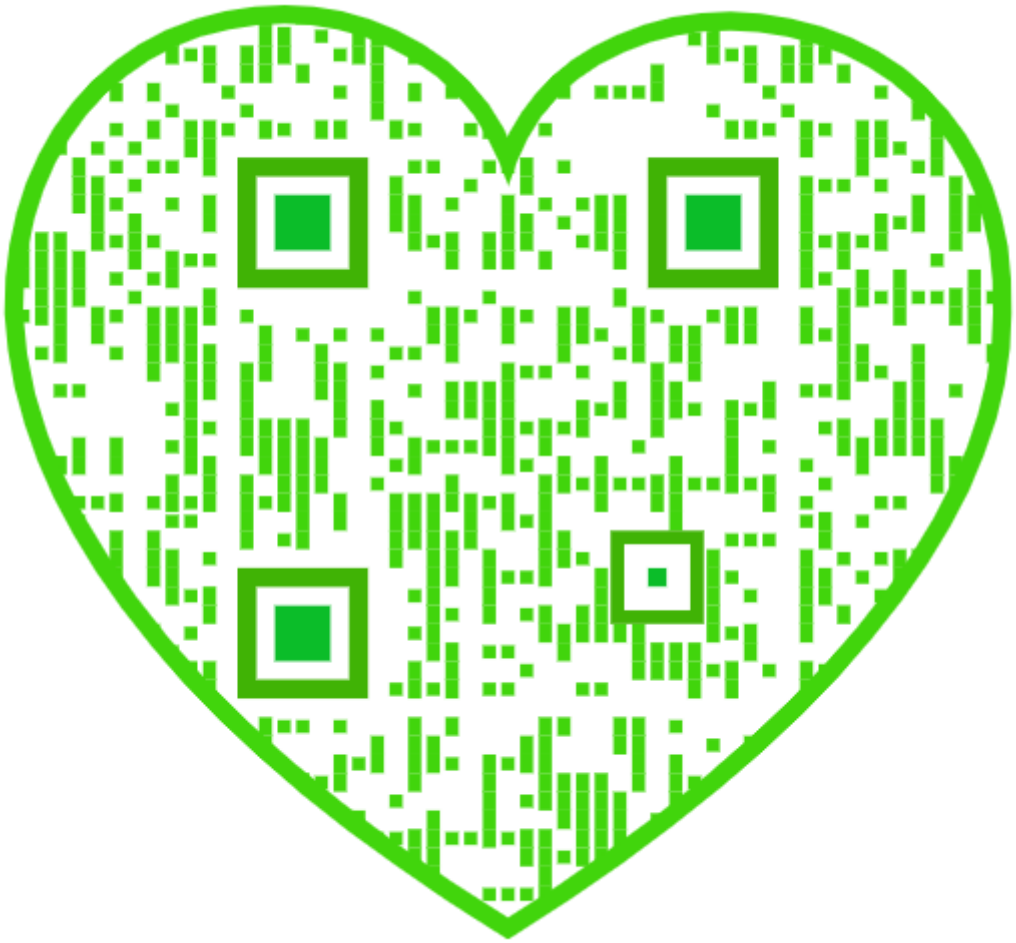
THE CHEMISTRY OF PIGMENTS

E. J. PARRY AND J. H. COSTE



THE CHEMISTRY OF PIGMENTS

BY

ERNEST J. PARRY, B.Sc. (LOND.), F.I.C., F.C.S.

AUTHOR OF "THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES," ETC.

AND

JOHN H. COSTE, F.I.C., F.C.S.

WITH FIVE ILLUSTRATIONS

LONDON
SCOTT, GREENWOOD & CO.
19 LUDGATE HILL, E.C.
1902

[*All rights reserved*]

TP936
P2

GENERAL

PREFACE.

The authors have in the following pages endeavoured to indicate the chemical relationships, composition and properties of most of the better-known pigments. During recent years they have given a great deal of attention to the examination of painters' colours, and have from time to time found some difficulty in obtaining reliable information on the subject. This led to a considerable amount of work in obtaining and examining specimens of pigments, and it was felt that the information thus gained might usefully be published.

Speaking generally, the plan of the authors has been to treat the various pigments in groups, allied chemically rather than chromatically. Motives of convenience have in some cases led to a modification of this scheme. The methods of manufacture of colours have been considered rather from the chemical than the technical point of view; it is not suggested by the authors that the present work is in any sense a manual of colour-making.

Analytical processes which, in most cases, the authors have by experience found suitable are described, and the nature of probable impurities,

104628

adulterations and other causes of inferiority pointed out, and numerous analyses of genuine and sophisticated pigments, for the most part by the authors, are given as illustrating the composition of these bodies. Preliminary chapters on colour and on the application of pigments have been added.

It is the hope of the authors that this work may be found of use by those who are called upon to use or examine pigments as a guide to the selection of those which are suitable, and the rejection of those which as a class or through individual inferiority are unsuitable for the class of work to be undertaken.

E. J. P.
J. H. C.

London, *October*, 1901.

CONTENTS.

CHAPTER I.

INTRODUCTORY.

Light—White Light—The Spectrum—The Invisible Spectrum—Normal Spectrum—Simple Nature of Pure Spectral Colour—The Recomposition of White Light—Primary and Complementary Colours—Coloured Bodies—Absorption Spectra *pages* 1 to 17

CHAPTER II.

THE APPLICATION OF PIGMENTS.

Uses of Pigments: Artistic, Decorative, Protective—Methods of Application of Pigments: Pastels and Crayons, Water Colour, Tempera Painting, Fresco, Encaustic Painting, Oil-Colour Painting, Keramic Art, Enamel, Stained and Painted Glass, Mosaic . . . . . *pages* 18 to 76

CHAPTER III.

INORGANIC PIGMENTS.

White Lead—Zinc White—Enamel White—Whitening—Red Lead—Litharge—Vermilion—Royal Scarlet—The Chromium Greens—Chromates of Lead, Zinc, Silver and Mercury—Brunswick Green—The Ochres—Indian Red—Venetian Red—Siennas and Umbers—Light Red — Cappagh Brown — Red Oxides — Mars Colours — Terre Verte — Prussian Brown — Cobalt Colours—Cœruleum — Smalt—Copper Pigments — Malachite — Bremen Green—Scheele's Green—Emerald Green—Verdigris—Brunswick Green—Non-arsenical Greens—Copper Blues—Ultramarine—Carbon Pigments—Ivory Black—Lamp Black—Bistre—Naples Yellow — Arsenic Sulphides: Orpiment, Realgar—Cadmium Yellow—Vandyck Brown . . . . . *pages* 77 to 181

CHAPTER IV.

Organic Pigments.

Prussian Blue—Natural Lakes—Cochineal—Carmine—Crimson—Lac Dye—Scarlet—Madder—Alizarin—Campeachy—Quercitron Rhamnus—Brazil Wood—Alkanet—Santal Wood—Archil—Coal-tar Lakes—Red Lakes—Alizarin Compounds—Orange and Yellow Lakes—Green and Blue Lakes—Indigo—Dragon's Blood—Gamboge—Sepia—Indian Yellow, Purree—Bitumen, Asphaltum, Mummy . . . . . *pages* 182 to 275

Index . . . . . *pages* 277 to 280

LIBRARY OF THE UNIVERSITY OF CALIFORNIA

THE CHEMISTRY OF PIGMENTS.

CHAPTER I.

INTRODUCTORY.

Colour phenomena may, broadly, be divided into two classes. In the larger and more important group they are due to the selective action of what we know as *coloured* bodies upon light, whilst in the smaller group they are dependent upon quite other causes, which, from the point of view of the present work, need not be touched upon. The colour effects produced by pigments belong entirely to the former class, and to intelligently understand the principles of colouring materials, an elementary but exact knowledge of the theories of light is necessary. In the present chapter the theoretical aspect of the subject is briefly referred to from this point of view, but no mathematical details are introduced, except where absolutely necessary for the comprehension of the point at issue.

Light.

Light is due to a series of intensely rapid vibrations of a medium which is assumed to be imponderable, and to pervade all space and matter. Such a medium is, of course, physically quite incomprehensible, but its existence must be assumed to satisfactorily explain the ordinary phenomena of light. These vibrations are transverse, that is, in planes at right angles to the direction of propagation of the beam. The vibrations in sound waves are, on the other hand,

longitudinal, that is, in the direction of the propagation of the wave. This hypothesis is known as the wave theory, or the undulatory theory of light, the vibrations evidently partaking of the nature of waves. Indeed they may be well illustrated by ordinary waves, and the distance between two successive crests is termed the *wave length*, whilst the distance from crest to trough is the *amplitude*. The intensity of the wave depends on the latter, whilst its specific character, as will be seen later, depends essentially on the wave length.

White Light.

The ordinary light of the sun, which we recognise as white light, is a mixture of innumerable vibrations of different wave lengths, or, what amounts to the same thing, of different colours. This is best illustrated by the classic experiment of Newton, which was undertaken by him to prove the proposition that "the light of the sun consists of rays differently refrangible" (Newton, *Opticks*, book i., prop. ii., theorem 2). This experiment may be briefly described as follows: Into a perfectly dark room (see Fig. 1) a beam of light is admitted through a small round hole, O, and in its path is placed a triangular glass prism P. The light falling on the prism is refracted or bent (as is always the case when light passes from any medium to any other of different density), and on being received on the screen Q it is seen that instead of a white spot we have an elongated band of different colours. This is the "spectrum" S.

The Spectrum.

This coloured band, which is called the prismatic spectrum, in order to distinguish it from that produced in another manner (*vide infra*), is composed of a series of colours, situated in the same order as are those in the rainbow, which owes its

existence to an action of this kind. As a matter of fact, every vibration of different wave length is refracted to a different degree, the rays of shorter being more refracted than those of longer wave length. Hence the fact that the colours in the spectrum merge gradually into one another, and although each separate position as we advance from one end to the other is of a different colour absolutely, we cannot, with the eye, enjoy such fine distinctions, so that we are compelled to separate the spectrum into arbitrary divisions in which the

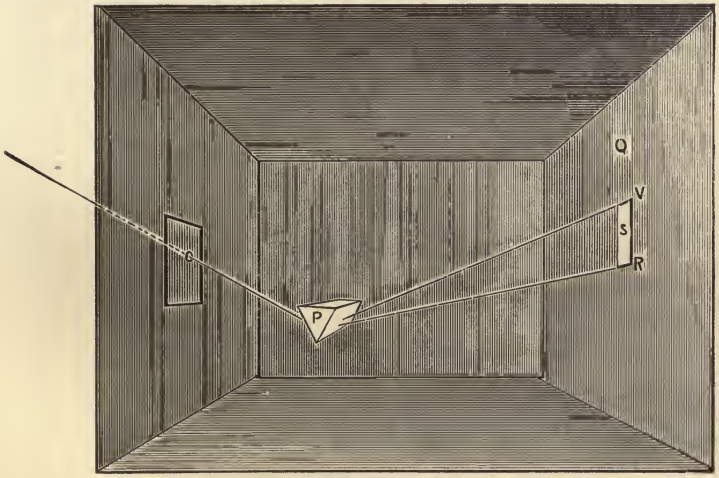


Fig. 1.

main colour is represented in its various shades. For convenience Newton divided the spectrum into seven parts, starting from the least refracted rays, as follows: Red, orange, yellow, green, blue, indigo and violet. Any other similar division is quite legitimate—such, for example, as the more extended—red, orange red, orange, orange yellow, yellow, etc., etc. To exactly define the spectral colours, as they are called, however, we need something more exact. We have this in the Frauenhöfer lines (so named from their discoverer), a series of fine dark lines which break the con-

tinuity of the spectrum of sunlight. As these dark lines depend on the existence of definite elements in the sun's atmosphere their position is absolutely fixed, and their positions having been determined with accuracy, they can be used as points of reference. The most prominent lines are those named from A to H, starting from the red end of the spectrum. These lines are reproduced as *bright* lines in the same position, when, for example, the element responsible for the given line is volatilised in a colourless flame. The D line (which is in reality two lines extremely close together), for example, is characteristic of the element sodium. If the visible portion of the prismatic spectrum, that is, from the red to the violet, be divided into 1,000 parts, the positions of these lines are as follows :—

A . .	0	E . .	363·11
B . .	74·02	F . .	493·22
C . .	112·71	G . .	753·58
D . .	220·31	H . .	1,000

The Invisible Spectrum.

Hitherto we have referred only to the visible spectrum, that is, the coloured bands which are produced when white light is decomposed by, for example, a glass prism. But it has been shown beyond doubt that heat waves are subject to many of the same laws as light waves, and it appears that the same class of vibration is responsible for the phenomena of heat and light. If a delicate thermometer be placed in the various parts of the visible spectrum, it will be found that, if we use a prism of, for example, rock salt, which absorbs practically none of the vibrations, the temperature varies with the portion of the spectrum in which the thermometer is placed. The maximum is obtained in the extreme red of the spectrum, and a gradual fall occurs till the extreme violet is reached. But if the thermometer be moved out of the

spectrum past the red an increase of temperature is noticed, a maximum being obtained just beyond the visible rays. These invisible rays, which are less refracted, and of greater wave length than the visible rays, are the dark heat rays. Beyond the violet is also another set of rays which are very highly refracted and of very small wave length, which are known as the ultra-violet or chemical rays. These are closely connected with many chemical effects and with fluorescence phenomena, and can, to a small extent, be rendered visible by special appliances. The spectrum, including the ultra-violet and ultra-red rays, may thus be divided into chemical, light, and heat rays.

The phenomena observed in heating a piece of iron will illustrate this matter. At comparatively low temperatures the slow vibrations in the mass are responsible for the emission of the longer or dark heat waves. As the temperature increases and the vibrations become more energetic, waves of shorter period are emitted, and at length the red of the spectrum appears and the iron mass assumes a dull red heat. As the temperature becomes more and more elevated the vibrations of shorter and shorter period appear and are added to the red, and finally all the colours of the visible spectrum are emitted, and the iron assumes a white heat.

The Normal Spectrum.

Usually, spectra produced by means of a glass prism suffer from two defects. Firstly, they are not quite pure, that is, the colours seen overlap to a small extent, and therefore the continuity of the pure colours is destroyed. Secondly, the position of each colour is not exactly in proportion to its wave length, and there is what may be called "crowding" in places. With very special appliances these defects may be almost entirely rectified, however, but by means of a diffraction grating we can produce a spectrum that is both

pure and normal. A diffraction grating is a system of very narrow, equal and equidistant rectangular apertures, usually employed in the form of a glass plate with an enormous number of parallel fine lines traced on it at equal distances with a diamond point, the two series being at right angles to each other. When a luminous centre is viewed through this, a central or direct image is seen, and on either side of it are several spectral fringes richly coloured with all the rainbow colours. For the theoretical considerations connected with the production of these diffraction spectra, the reader is referred to advanced text-books on optics. It here suffices to say that there is no overlapping of the colours, and whilst the intensity of the spectrum is small, it has the advantage of being quite pure; and, further, if the diffracted light is at right angles to the surface of the grating the spectrum is normal, that is, the position of each ray is in exact proportion to its wave length. The importance of this is seen by the fact, that not only, as mentioned above, is there some overlapping in ordinary prismatic spectra, but the *irrationality of dispersion*, as it is called, is so great in some substances that the order of the colours is actually reversed. The relative space occupied by the various colours in a prismatic spectrum depends on the prism, but for ordinary glass prisms made of *crown* glass the following may be taken as representing the relative spaces. Those of the normal spectrum are given as well. In each case the spectrum is assumed to be divided into 1,000 parts:—

	Prismatic Spectrum.	Normal Spectrum.
Red	0 — 150	0 — 330
Orange-red	150 — 195	330 — 435
Orange	195 — 210	435 — 460
Orange-yellow	210 — 230	460 — 485
Yellow	230 — 240	485 — 500
Green-yellow	240 — 345	500 — 575
Green	345 — 450	575 — 690
Blue	450 — 805	690 — 880
Violet	805 — 1,000	880 — 1,000

The Simple Nature of the Pure Spectral Colours.

The true spectral colours are of a simple nature, that is, they cannot be further decomposed into other colours as white light can. This can be shown with great ease in the following manner. A narrow slit, A′, is made in a shutter parallel to an opening, A, in the screen, S, which can be moved as desired. The beam of light passing through A is allowed to pass through a lens to render the emergent rays parallel, and to fall on a prism, P. The spectrum appears on the screen, and any desired portion can be made to pass through the slit, A, and to again fall on a prism, Q, and after

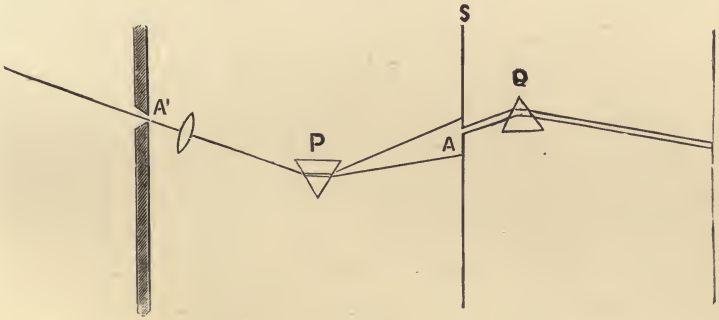


Fig. 2.

traversing this on to the screen, T. It will be seen that the image on T is always identical with the light which is allowed to pass through the slit A ; hence the light cannot be further decomposed.

The Recomposition of White Light.

The above experiments are of an analytical nature, but the reverse experiments are easy to perform, and white light can thus be synthesised from its components. There are several methods of effecting this synthesis, amongst which the following may be mentioned. A beam of white light

may be passed through a prism and so decomposed into its component coloured rays, which are then allowed to fall on a prism of the same nature in the reverse position, when the refraction in the reverse direction takes place, and the emergent beam is white again.

A second, but rough-and-ready method of showing this effect is to paint a circle of cardboard in sections with the seven principal spectral colours, and rotate it rapidly round an axis passing through its centre. Owing to the phenomenon of the persistence of vision, the impressions of the colours are more or less superimposed, and an approximation to white is the actual colour observed.

Primary and Complementary Colours.

The popular idea that the colours red, yellow and blue are "primary" colours on account of the fact that no human eye has been able to detect in them two different colours, whilst all other colours contain at least two primary colours, is quite erroneous, and is based on visible results obtained in the mixture of pigments and the transmission of light through coloured glasses. The interpretation of these phenomena is of a different nature, and it is more correct to regard each of the spectral colours as primary and elementary. It is true that the theory first propounded by Dr. Thomas Young, that there are three primary colour sensations, has received universal acceptation. This theory propounds that there are three chief elements in colour sensations, that is, three distinct physiological actions, which, by their various combinations produce all our sensations of colour. Each of these primary colour sensations is excited by wave lengths covering a wide range, but possesses its maximum excitability for rays of definite wave length. These points of maximum sensibility are in the green near Frauenhöfer's line

b, in the extreme red, and in the extreme violet. The impression of white light on the retina of the eye may be produced by various combinations; the results are identical to the eye, but the differences in the combinations are at once perceived when the light is spectroscopically analysed. Thus the following pairs of colours, when combined, give white light:—

Red	Blue-green.
Orange	Blue.
Yellow	Violet-blue.
Greenish-yellow	Violet.
Green	Pink (red-violet).

Each of the spectral colours which in combination with another colour yields white light is said to be *complementary* to that colour; thus yellow and blue are complementary colours, and green and red (within the limits as shown above) also. The term secondary colour is applied to the colour resulting from the mixture of two primary colours, such as red and blue, which produce a violet or purple, and tertiary colours are those which result from the mixture of two secondary colours. These terms, however, are exceedingly arbitrary and, consequently, not very scientific.

Coloured Bodies.

For convenience we may study the substances which we know as "coloured bodies," under two headings—(*a*) opaque bodies, (*β*) transparent bodies. The former owe their colour to the phenomenon known as irregular reflection, and to the fact that this irregular reflection is usually of a selective nature. The ordinary phenomena of reflection which obey the two well-known laws—*viz.*, (1) that the reflected ray lies in the plane of incidence; (2) that the angle of incidence and the angle of reflection are equal—are known as regular reflection. These phenomena do not render objects visible

at all, but merely give images of *surrounding* objects. Indeed, the reason that an ordinary mirror surface is visible is that a small quantity of *diffused* or irregularly reflected light is emitted. This diffused or irregularly reflected light consists of rays reflected in all directions, which do not apparently obey the two above-mentioned laws owing to at least two reasons: (1) on account of the small irregularities of surface, and (2) on account of partial absorption and internal reflection; and to these the visibility of the object is due. Now, a body which (irregularly) reflects all the rays of the spectrum in the same proportion as they are present in the incident light will appear of the same colour as that light. The majority of bodies, however, reflect some rays in greater proportion than others, their colour being due to the mixture of reflected rays. From these remarks it will be seen that the colour of a given body depends on two chief circumstances, (α) the inherent selective action which a given body has for definite rays, which is constant for a given body; (β) the composition of the light falling on the body. The colours we assign to given bodies are always those which they possess when the incident light is white. Thus a body which absorbs the blue, green and yellow rays of the spectrum and reflects the red rays presents the appearance we know as red when the incident light is white. But when the majority of red bodies are examined in, for example, the yellow light of the sodium flame, their colour is a dull brown, on acccount of the fact that the amount of red rays falling on the body is so small that the reflected light contains a correspondingly few red rays, and the observed colour is made up of the small number of rays of different colours which the body is able to reflect. The usual form, from our point of view, of opaque-coloured objects with which we have to deal is that of coloured powders. But to discuss these it is necessary to understand the cause of colour

in transparent bodies. A transparent body when examined by transmitted light is coloured if it is more transparent to some rays than to others, its colour depending entirely on the nature of the transmitted rays, or, in other words, is due to the absorption of certain rays dependent on the nature of the substance itself. Many transparent substances appear of different colours when different thicknesses are examined. For example, a solution of chromic chloride is green when light is allowed to traverse a thin layer of the solution, but when the thickness of this layer is increased the colour observed is a reddish brown. Such substances are termed *dichroic*. In such a case as this, certain rays are only partly absorbed, and the substance must be of a certain thickness before the absorption is complete, the colour, of course, being due to the residual transmitted rays. When two pieces of different coloured glass are examined together by transmitted light, the colour observed is not by any means the mean of the two, nor is it the sum of the two colours. As the colour is due to the *transmitted* rays only, it is dependent on those rays which both pieces of glass allow to pass. Thus a piece of red glass allows light to pass through which consists almost entirely of red rays. Green glass, on the other hand, allows practically no red rays to pass through. Hence a combination of red and green glass will be almost opaque to the observer. Again, light transmitted through blue and yellow glasses will in general be green—not because blue and yellow mixed form green, as is popularly said; but because most yellows and blues when spectroscopically analysed are found to contain a large amount of green rays, and it is the green rays which both these colours transmit to the almost entire exclusion of the other rays. Very few transparent bodies are perfectly opaque to any rays. These are usually transparent to a very high degree for that one set of rays which dominates the observed colour, and allow other rays

to pass in small amount. These other rays, of course, modify the colour according to their nature and quantity.

We may now return to the subject of coloured powders, which, of course, form the vast majority of pigments in everyday use. In a coloured powder every small particle must be regarded as a small transparent body capable of rendering light coloured by selective absorption in the sense we have just detailed. It is quite true that powdered pigments when taken in bulk are very opaque indeed, but nearly every substance when examined in extremely thin layers is found to be fairly transparent, and upon this transparency their colour effects depend. When white light falls on such a powder a small portion of it is reflected from the outside surface of the particles; the remainder penetrates the particles and undergoes reflection at some of their surfaces of separation. The small portion which is reflected from the immediate outer surface is white, as no absorption has occurred, but that which is reflected after absorption is that which determines the colour; and since given substances possess definite selective ability, the reflected rays are fixed for a given substance in a given physical condition. It now becomes easy to understand the reason of the alteration in the colour of mixed powders. A mixture of green and blue powders does not appear green because green is the colour situated between the blue and yellow in the spectrum, but because the blue pigment absorbs the red, orange and yellow rays and the yellow absorbs the violet and blue. Hence the only colour which is reflected by both of them is the green, which reaches the eye as such. Many common phenomena of the painter's art are easily explained in the light of the above statements. For example, we all know that a coarsely ground powder is more deeply coloured than the same powder very finely ground. The quantity of light returned at each successive reflection depends on the number of

reflections. If the particles are large the light has to penetrate so much the deeper in order to undergo a given number of reflections, and more light will therefore be absorbed, and the resulting colour will appear deeper. The finer the particles the more white light is there reflected at the surface before any penetration occurs. A very good example of this is the white froth of a deeply coloured liquid. Again, the reflection at the surfaces of particles is much weakened by interposing between them a fluid whose refractive index is nearer to that of the particles themselves than that of air is. Pigments are thus rendered darker by wetting them with water, and still more so by using the highly refracting oils. Much less white light is reflected, and the colour appears far darker. This explains the characteristic differences between crayon drawings, water colours, and oil paintings (*vide infra*).

We have said that the light reflected from the extreme outside surfaces of particles is white, but there are certain exceptions to this rule, and some bodies appear to reflect certain rays by selection in preference to others. Such bodies are said to possess *surface colours*. Many of the aniline dyes are of this nature, and appear of different colours when examined by transmitted and by reflected light. The colour when seen by reflected light is determined (1) by the normal irregular reflection, (2) by the abnormal reflection of the selected rays which have been entirely refused admission into the particles. The colour examined by transmitted light is determined (1) by the absence of the abnormally reflected selected rays mentioned above, (2) by the rays which are absorbed in the body of the particles. A very well marked example of this is the aniline colour, fuchsine. This appears of a metallic green colour by reflected and of a rose red colour by transmitted light. Incidentally we may mention, as illustrating the dependence of colour phenomena on external circumstances, that the solution is peacock blue

when examined through a polarising prism, but the explanation of this is outside the scope of the present work.

The proper study of colour effects and mixtures is dependent on a knowledge of the exact selective power of various substances. This property is only to be exactly understood by the examination of the *absorption spectra* of the bodies in question. When a pure solar spectrum is examined, it is seen to be crossed by a number of dark lines, usually known, as mentioned above, as Frauenhöfer's lines. Each wave produces its own image of the slit of the spectroscope in its proper position, according to its refrangibility, and in a spectrum of an ordinary incandescent body, which is not traversed by any dark lines, the wave lengths differ in so gradual a manner that the various images are extremely close together and the spectrum appears *continuous*. We must not assume, however, that light rays of every possible refrangibility are present because a spectrum is continuous. It is more correct to say that all wave lengths are present, within the limits of the resolving power of the best instruments we possess; and were it possible to construct spectroscopes of infinitely greater resolving power than the best we now possess many continuous spectra might become discontinuous. The black lines observed in the solar spectrum indicate the absence of the rays of refrangibilities corresponding to the positions of those lines. To be correct, we should not say that these rays are completely absent, but they are so nearly so that they appear black by contrast with the other brilliant illumination. These dark lines are found to be in the exact positions of the brilliant bands emitted by certain definite incandescent vapours. For example, the well marked D line of the solar spectrum (or, more correctly, D *lines*, as powerful spectroscopes will effect this resolution) is identical in position with the brilliant yellow sodium line seen when sodium vapour is incandescent. The explanation

of these dark lines is that the inner mass of the sun emits the light which gives a continuous spectrum. This, however, has to pass through certain cooler vapours on the outer surface, and these absorb each its own special rays almost entirely, thus accounting for the absence of these rays in the solar spectrum, as we see it. In this manner a very large number of elements have been shown to be present in the sun's vapour.

These continuous or discontinuous spectra are produced by luminous bodies, but colouring matters are not in themselves luminous, and to produce their absorption spectra we must allow light to traverse a glass vessel containing a solution of the colouring matter, before reaching the slit of the spectroscope. The spectrum now observed will be found to be traversed by one or more dark bands of varying width, the colour bands observed being constant for definite bodies under given conditions. The absorption spectra of bodies may be graphically represented either by shading the dark bands according to the degree of absorption on a continuous spectrum diagram, or, better, by indicating the spectrum by a horizontal line (abscissa), and the intensity of the absorption at each point by means of vertical distances from the abscissa (ordinates). The resulting curve at once gives an extremely comprehensive grasp of the properties of the colour. It will now be convenient to give an account of the absorption spectra of a number of bodies of various colours, starting, say, from the red end of the spectrum.

Azorubine.—This body is one of the coal-tar dyes of the diazo series, known chemically as *sodium naphthalene sulphonate azo-α-naphtol sodium sulphonate.* It is a full crimson colour, suppressing practically all rays except the extreme red (Fig. 3, 1).

Scarlet R belongs to the same group of compounds, and is *sodium xylene-azo-β-naphtol sulphonate.* It is a fine scarlet

colour, and its absorption spectrum shows that it allows practically nothing but the red and a portion of the yellow-orange rays to pass (Fig. 3, 2).

Alizarin.—This body is the essential colour-bearer of the well-known madder plant, but is now practically entirely produced synthetically from anthracene, one of the hydrocarbons present in coal tar. It is a *dioxyanthraquinone.* This fine red colour gives absorption spectra, which do not materially differ if the solvents are neutral, but which are by no means identical when acids or alkalies are added. Several of these are given here, from which it will be seen that all rays as far as the D line are fairly freely transmitted in all cases (Fig. 3, 3).

Eosin.—Typically pure eosin of commerce, which is usually sold as Eosin J, is the hydrated potassium salt of *tetrabromo-fluorescein*, of the formula $C_{20}H_6Br_4O_5K_2 + 6H_2O$. Mixtures of this body with the analogous dibromo-compounds are sold as Eosin 5 G, and have a more orange shade, and various closely related compounds of lighter or darker shades are common articles of commerce. The appended spectrum is that of the typical compound in (α) concentrated, (β) dilute alcoholic solutions (Fig. 3, 4).

Tartrazine.—This well-known colour is the sodium salt of *disulpho-diphenylizine-dioxytartaric acid.* It is an orange yellow powder which produces a fine yellow colour with a reddish tint. *Picric Acid*, or *trinitrophenol*, is a typical colour yielding a much yellower spectrum than tartrazine. The two are here illustrated (Fig. 3, 5).

Acid Green is the typical name of a number of coal-tar greens, which are sulphonic acids of the various aldehyde greens. Of these the ordinary Helvetia green is one of the most common. The spectrum given shows that the whole of the red and yellow and much of the violet is totally extinguished, with the result that a brilliant green (with blue in it) results (Fig. 3, 6).

Indigo.—The spectrum yielded by indigo extract varies to a small extent according to the exact method of preparation of the extract. But these variations are only slight, and the chief feature of a typical extract, which is shown below, is the almost complete extinction of the red-yellow rays and the extreme violet (Fig. 3, 7).

Methyl Violet.—The last spectrum we shall here consider is that of methyl violet, one of the coal-tar violets, whose chemical relationships are expressed by the name *pentamethyl pararosaniline hydrochloride.* The total extinction of nearly the whole of the red, all the yellow and all the green rays is the characteristic of this spectrum (Fig. 3, 8).

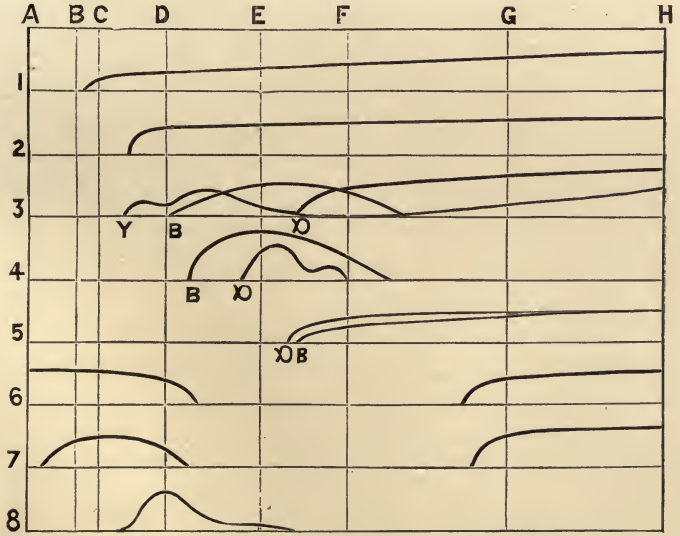



Fig. 3.

3. α Alcoholic solution.
   β Alcoholic ammoniacal solution.
   γ Aqueous ammoniacal solution.
5. α Tartrazine.
   β Picric acid.

CHAPTER II.

THE APPLICATION OF PIGMENTS.

In deciding the relative suitability of pigments for any particular case two sets of circumstances must be taken into consideration: on the one hand, the purpose for which the pigment or pigments may be required, whether purely artistic, decorative or protective, and the conditions under which this purpose must be fulfilled; and, on the other, the nature of the pigments and of the media and methods of application at the worker's disposal. These circumstances having such an important bearing on the chemistry of pigments, we have thought it advisable to consider them before proceeding to the systematic description of the pigments themselves.

I.—USES OF PIGMENTS.

(A) Purely Artistic Uses.

These include all those various methods of depicting objects and events in colours which have been recognised as most suitable when accuracy of representation, whether imitative or suggestive, has been the principal object sought to be attained. It is obvious that this is the highest use to which colours can be put, and in many respects the most exacting in its requirements, the more general of which, as applying equally to all branches of pictorial art, we will now consider.

Whatever surface may be adopted for the reception of the picture, and in whatever manner it may be decided to apply and fix the colours on that surface, it is evident, in the first place, that the relations of surface and colour must be such that the masses of colour applied may be distributed in any form that is necessary for depictive purposes, and, whether the work is in natural colours or monochrome, shall be capable of all gradations of shade or intensity, from the full density of the colour to the merest suggestion of the same.

In order that this quality of "workability" may be possessed in the highest degree, it is necessary that the pigment be in a very fine state of division, and uniformly diffused throughout the medium by means of which it is applied, and that some means of dilution can be adopted, either by the addition of a white pigment in the case of "body colour," or by increasing the proportion of medium or the application of the colour in very thin layers in those cases in which the colour is used as a "stain" or "glaze". This fine state of division is obtained by various processes of crushing, grinding, occasionally by roasting and washing or levigation. The latter method is particularly valuable, as particles which could not be separated by the finest sieve can be suspended in water and the finer matter, after the coarser particles have settled to the bottom of the vessel, run off with the water and allowed to slowly deposit, the coarse particles being again ground. All these processes of preparation of powders are described in various technical works, and need not be considered at length. It is not now the general custom for artists to prepare their own colours, though before the rise of a special industry this was necessarily the case. In this respect, at any rate, modern artists are more fortunate than their predecessors, as doubtless specialised machinery is more effective than

the more primitive appliances of earlier ages, and time is not wasted in purely mechanical operations. It is possible, however, that in some other respects the wholesale preparation of artists' colours is not an unmixed boon. The question of media or colour vehicles will be discussed in another part of this chapter; for the present it is sufficient to predicate of the medium that it shall have no immediate appreciable effect on the appearance of the colour, and in most cases that after the colour is effectually fixed on the receptive surface its tint shall remain unaltered, or that in special cases the effect shall be certain and easily estimable.

Granted the possession of the quality of workability, it is necessary that the colours at the artist's disposal be iris-hued, capable either separately or judiciously mixed of imitating the colour or the colour effect of any object which the eye has seen or can conceive. Unless this is so artistic effort must be confined to monochrome (which, though giving considerable scope for a master of form and light and shade, has, it must be confessed, much the same effect on the eye as a Gregorian chant in music, or a very severe adherence to a very obvious metre in poetry, has on the ear), or to a very crude colour scheme which is less pleasant and certainly less artistic than monochrome. In this respect, so far as the representation of objective effects are concerned, our known pigments leave very little to be desired, as an examination of the works of the great pre- and post-Raphaelites (and Raphael himself) of the Italian schools, of the Dutch school, especially some of the still-life examples, and, though last, not, in many respects, least, of our great English landscape painters, and of those two masters of atmospheric effect, Claude and Turner, will convince one. The suggestion of the *subjective* phenomena of interference and diffraction colours has indeed not presented insuperable difficulties to some of our colourists. It is not, however, sufficient for the

highest kind of artistic work that colours should be capable of easy application to the prepared surface and be sufficiently diverse and brilliant for purposes of imitation, but, in justice to the labours of the artist, they must, under reasonable conditions, be *permanent*. In this respect the artist is, relatively to the poet or musician, very unfortunately placed in regard to posterity; the effect sought to be produced by either of the latter is entirely independent of the manner of reproduction. The writings of Homer, Shakespeare or Milton, the musical compositions of Palestrina, Purcell, Ahn or Mozart, and those fragments of ancient music we possess are not only (except for corruption of text or score) in the same verbal form as the original copy issued from the author's hand, but, thanks to writing, musical notation and printing, capable of indefinite reproduction. By reason of this fact there seems no reasonable possibility of such works being either lost or, saving for alterations of taste and habits, failing to produce the same emotions and sensations as they have always been capable of doing. With the artist things are entirely different, he appeals to the feelings, not through the ear, nor through the eye as a mere signalling instrument, but through the eye in all its powers of conveying sensations of form, colour, light and shade; his work, as laborious, as poetical as that of the writer or composer, cannot be reproduced in such a way as to convey its full effect, and consequently he can only appeal to a limited number of people (and only in one place). Not only is this the case, but he is working with materials the entire suitability of which can never be satisfactorily determined, for whereas we can decide that such a work is fading, or the surface cracking, or the high lights going, and so being lost to posterity, we can never be sure that another work now in good preservation may not in the future show signs of such decay. The materials used by artists are also only perman-

ent when properly kept, so the safe custody of the *one* only example of each work of the artist becomes a matter of the highest moment.

The ideal of permanence required of artists' colours is very comprehensive. The surface must not only remain intact in spite of the action of air, moisture, light and some variations of temperature (not usually great), but all the colours must retain to a very great degree, if possible to the end of time, their original tint, however delicate. The bright colours and the high lights must retain their brilliance, and the darker colours and shadows their obscurity, or the contrast of light and shade, the chiar'oscuro as it is called, will be destroyed, and the objects which, when the picture left the painter's hands stood out, as it were, from the picture, and those which were in the distance, appear to be but little separated, and the whole seems flat and lacking in atmospheric effect.

That this permanence of colour and shade has been very closely approximated to by many old masters is shown on an examination of their works. The earliest examples in the National Gallery are a series of portraits, either Greek or Græco-Roman, taken by Mr. Flinders Petrie in 1888 from mummy cases discovered in an ancient cemetery at Hawara in the Fayyûm, Egypt. Ten of these are painted on wood panels in the encaustic method, the remaining one being apparently in tempera on canvas; this specimen is not in very good preservation, rather the result of rough usage than natural deterioration. The others are still pleasing looking, the flesh colours being fairly good, and the white used for some of the draperies and high lights, two shades of (Tyrian?) purple, blue and crimson drapery, blue, red and green stones, set in gold, and other gold ornaments retaining sufficient of their original brilliancy to be convincing. Altogether, these ten pictures well illustrate the permanence of colours in so inert a medium as wax, though it must be

borne in mind that from the nature of the case the portraits, being preserved in the dark and in the dry atmosphere of Egypt, had everything in their favour. It remains to be seen what effect the light of a gallery and our moister climate will have on them. A painting by Margaritone (died 1293), in the conventional Byzantine style, of "The Virgin and Child, with Scenes from the Lives of the Saints" (No. 564) is not at all satisfactory. The colours are very dingy, and in some cases absolutely changed beyond recognition. The picture is in tempera on linen fastened to wood, and it is probable that part of the dark appearance is due to the unsatisfactory medium used. A painting—school of Giotto (*circa* 1330), who introduced white of egg as a medium—of "The Coronation of the Virgin" (No. 568) is still in very good preservation. The iris-hued wings of attendant angels, a green and a scarlet, still look fairly bright. Another painting of the same subject by Orcagna (died 1368), in which a great many figures are represented, shows such varied colours as crimson, scarlet, green and blue in very good preservation, and some very varied and pleasing flesh tints, from the delicate pink of the principal figures to quite a swarthy sunburnt hue. The swords in the hands of some of the saints, however, look very black, probably owing to serious changes in the pigment used. "A Baptism" by Taddeo Gaddi (died 1366) shows the following colours: two purples, crimson, a bright red, a colour like raw sienna, a sage green, blue, and two flesh colours, coarse and delicate, and the steel of a sword, all but the latter satisfactory. A "Virgin and Child" (No. 283) by Gozzoli (died 1498) shows good flesh tints, and two goldfinches still looking well coloured. His "Rape of Helen" (No. 591) shows good flesh colours, scarlet and blue; the landscape, with sea forming the background of this, is fairly good, but the green (probably vegetable) of the trees is very dull. Sandro Botticelli (died

1510) is represented by six pictures, all in tempera: No. 275, "The Virgin and Child, St. John Baptist and an Angel," is perfect in colour, the principal colours being delicate and swarthy flesh tints, and gold (brocade). No. 626, "Portrait of a Young Man in Brown Dress and Light Red Cap," is characterised by a rather tallowy (perhaps accurate!) flesh colour and a fine red. No. 915, "Mars and Venus and Four Young Satyrs," shows a very wide range of colours; very varied flesh tints, delicate for Venus, swarthy for the satyrs, white, gold, crimson, steel (armour), a reddish-brown conch shell and the dark rich green of the myrtle, a very fine picture. By the side of this is a picture (No. 651), "Venus, Cupid, Folly and Time," by Bronzino (died 1572) in which varied flesh tints, blue drapery, a russet apple (of Discord), red roses, a crimson cushion and the white doves of the Paphian goddess appear with a remarkable freshness. "A Virgin and Child" and a "Virgin Adoring the Infant Christ," by Lorenzo di Credi (died 1537), show a brilliance of colouring both of the figures and drapery and of the landscapes in the distance which time would have done well to soften, though in their way they are perfect. The "Portrait of Julius II." (No. 27), "St. Catherine of Alexandria" (No. 168), the Garvagh and Ansidei Madonnas and the ancient copy of the Bridgewater Madonna of Raphael (died 1520), "The Holy Family" (No. 4), "Venus and Adonis" (No. 34) and "Bacchus and Ariadne" (No. 35) of Titian (died 1576), "The Portraits of Jean Arnolfini and His Wife," by Jan Van Eyck (one of the earliest oil painters), painted in 1434, and many other works of masters of the early Italian and Flemish schools might be quoted as examples of beautiful fresh colouring, retaining, so far as may be judged, correct relationship of tone; but as this is a work rather on the materials used by artists than on their works, the mention of a few works by masters of light and shade and atmospheric effects, which would be

entirely marred by the fading of dark masses or the deterioration of high lights, must conclude this examination of pictures which have stood the test of time. The portrait by (and of?) Andrea del Sarto, Andrea senza errori (Andrea without faults) as he is called, would, if the beautiful soft light on the cheek or the white of the shirt were to darken, or the shade over the rest of the face and the darker background fade, be a dull, flat picture, though still beautiful, instead of being, as it is, *perfect*. The "Agony, after Correggio," with its peculiar illumination of the two figures in the darkness, requires absolute permanency in the high lights. The "Walk to Emmaus," by Lelio Orsi (died 1586), is another early work in which the whole effect is due to the chiar'oscuro: a burst of light through a dark sky lights the figures, throwing the folds of their garments and their faces into violent relief and reflecting gleams from a dagger hilt and the top of a walking stick. The later examples of Rembrandt, especially the marvellous "Adoration," with its natural and supernatural illumination, the heavenly light from the Child and the dull glimmer of the shepherds' lantern; of the Dutch landscape painters (especially Hobbema); of the French landscapists, Claude Lorraine ("Gelée") and Gaspard Dughet ("G. Poussin"), nearly all works depending for their highest beauty on very subtle schemes of light and shade and atmospheric effect, most of them over two centuries old, tend to show that it is possible to produce works of a very high degree of permanence both of colour and of tone. At the same time it must be admitted that some of the colours used by the earlier masters, as, for example, bitumen, were highly unsatisfactory both as permanent colours and on account of their injurious effect on the surface; and again, possibly, a process of natural selection has weeded out many once beautiful works from the front rank and turned them into the "speculative pictures" and "doubtful old masters" of the auction room and the would-

be art patron. It is, notwithstanding, a matter of great regret that we do not know more of the methods both of preparation and working of the old masters. That we know so little is not a matter for surprise; the secret process is not yet dead in chemical works (though it is usually a secret shared unconsciously with most other similar works) and the whole tendency of the middle ages, a tendency not seriously modified by the Renaissance, was for members of a guild or confraternity (of craftsmen) to keep their methods very secret, the master not always fully initiating his pupils, far less trusting his methods to paper or to his fellow, and rival, artists. Though in many ways to be regretted this is very natural on the part of those who had probably with great labour prepared their colours and discovered secrets they did not reveal. The fact, however, remains that of the methods of the ancients very little is known; to attempt a chemical examination of the works of acknowledged masters, involving as it would their destruction or serious mutilation, would be, apart from pecuniary considerations, an act of most atrocious Vandalism and would probably be entirely unsuccessful, both on account of the small amount of colour actually applied to the surface and of the difficulty of such examinations, particularly when it is desired to examine the nature of the medium employed. It is, to an extent, possible to form some idea as to the colours used on a certain picture, but this does not always, even if the conjecture be correct, convey much information, as permanence may be affected by the presence or absence of accidental impurities and depends on the pigment, the medium and the surface, even supposing conditions of preservation to be the same. The study of ancient pictures principally serves to remind us that it is possible to obtain and to apply colours that will last for centuries and still present to the eye such well-known hues as those of human flesh, of sea and sky, and of those animate

and inanimate living things which we know have not altered, and this not merely in a conventional manner (as the picture writing of certain ancient nations), but with that force of imitation or suggestion which almost convinces the eye of their reality. This test of the fidelity of colour of natural objects (making due allowance for the bluish flesh of one period, the brown tree of another, and other obvious mannerisms) seems, where applicable, the fairest to apply in judging of the permanence of colours *as colours;* the test of the conviction produced by arrangements of light and shade the best for that kind of permanence which is the result of fixity of intensity or that quality which alone would appeal to the colour-blind.

In the absence of this information concerning the permanent pigments of the earlier painters, and in face of the lamentable condition of many modern pictures (particularly those of Stothard, and, it is to be feared, some of Turner's and Landseer's), the desirability of an extended series of experiments on the action of light, air, moisture, heat and products of combustion is evidently great. Such experiments should include an examination of many (analysed) specimens of each pigment with a view to determining the influence of impurity and of variation of composition, and of the specimens used in different media on such surfaces as are generally considered suitable for the several media. So far as the modern and beautiful method known as "water colour," in which our countrymen have always excelled, is concerned, some most highly interesting experiments have been carried out in a manner remarkably free from empiricism by Dr. W. J. Russell and Captain (now Sir) W. de W. Abney, who in 1888 presented a report to the Science and Art Department "On the Action of Light on Water Colours". The interest of the report is enhanced by the circumstance that these gentlemen were advised and supplied with colours by a

OPEN TUBE.

Name of Colour.	14th August, 1886.	March, 1888.	Remarks.[1]
Carmine	Gone	Gone	—
Crimson Lake	Gone to 7	Gone	—
Scarlet Lake	Pink gone, Vermilion left	Gone	—
Vermilion	No change	Gone black	—
Rose Madder	No change	Faded to 4 and bluer	—
Madder Lake	No change	Sl. faded	—
Indian Red	No change	No change	—
Venetian Red	No change	No change	—
Brown Madder	Changed to 4	Faded to 3	—
Burnt Sienna	No change	No change	—
Gamboge	Faded to 2	Faded to 7	—
Aureolin	No change	Faded to 4	—
Chrome Yellow	No change	No change	—
Cadmium Yellow	No change	Gone	—
Yellow Ochre	No change	V. sl. faded	—
Lemon Yellow	No change	No change	—
Naples Yellow	Faded to 5	Gone	—
Indian Yellow	Faded to 2	Faded to 6	—
Raw Sienna	No change	No change	—
Emerald Green	No change	Sl. Brown	—
Terra Verte	No change	No change	—
Chrom. Oxide	No change	No change	—
Olive Green	Blue gone	Gone brownish pink	—
Antwerp Blue	Paler	Gone Green	Blue revived
Prussian Blue	A little lighter, no green	No change	—
Indigo Blue	Gone to 4, all lighter	Faded to 8	—
Cobalt Blue	No change	No change	—
French Blue	No change	No change	—
Ultramarine Ash	No change	No change	—
Leitche's (Cyanin) Blue	V. sl. faded	No experiment	—
Permanent Blue	No change	Faded to 4	—
Payne's Grey	Gone red to 7	Gone	—
Violet Carmine	Red nearly gone	Bleached to 6	—
Purple Carmine	Red nearly gone	Bleached to 6	—
Purple Madder	Faded to 7	Faded to 8	—
Sepia	Faded to 1, all lighter	Faded to 8	—
Vandyke Brown	Faded to 4	Gone	—
Burnt Umber	No change	V. sl. faded	—

Brown Pink	Gone to 3	Faded to 7	—
Indian Yellow and Rose Madder	Gone pink to 6, yellow going in all	Gone pink	—
Rose Madder and Raw Sienna	No change	V. sl. yellowed to 5	—
Raw Sienna and Venetian Red	No change	No change	—
Venetian Red, Madder Red and Ind. Yellow	Redder in all	Sl. faded, gone pink	—
Vermilion and Chrome Yellow	No change	Darkened	—
Indian Red and Rose Madder	No change	No experiment	—
Indian Yellow and Rose Madder	Part faded, yellow gone to 3	Gone pink	—
Burnt Sienna and Naples Yellow	Browner	V. sl. faded	—
Indigo, Ind. Yellow, Raw and Burnt Sienna	Gone reddish in all	Gone red	—
Indigo and Gamboge	Gamboge going in all	Faded to 6	—
Prussian Blue and Gamboge	Yellow going	Gone blue to 7	—
Burnt Sienna and Antwerp Blue	Sl. redder	Gone sl. brown	Blue revived
Raw Sienna and Antwerp Blue	Sl. redder	No change	—
Prussian Blue, Raw and Burnt Sienna	Blue gone	Brown	Blue revived 1 to 3
Indigo and Vandyke Brown	Vandyke Brown going, all gone as far as 2	Faded to 5	—
Prussian Blue and Burnt Sienna	Blue gone	Gone brown	Blue revived
Prussian Blue and Raw Sienna	Browner	Gone brown	—
Indigo and Raw Sienna	Reddish	Gone yellow to 5	—
Indigo and Burnt Sienna	Sl. browner	Gone brown	—
Leitche's Blue and Burnt Sienna	Browner	Gone brown	Blue revived 1 to 5
Leitche's Blue and Raw Sienna	Browner	Gone brown	—
Indigo, Raw and Burnt Sienna	Browner	Gone red	—
Prussian Blue and Vandyke Brown	Blue, and fading to 3, Vandyke Brown gone in all	Blue gone, a little brown left	Blue revived
Indigo and Venetian Red	Redder	Gone red	—
Prussian Blue and Indian Red	Gone red in all	Gone red	Blue revived
Cobalt and Indian Red	No change	No change	—
Prussian Blue and Venetian Red	Gone red in all	—	—
Antwerp Blue and Rose Madder	Gone pinkish	Gone pink	—
Prussian Blue and Crimson Lake	Red all gone, blue lighter	Gone blue	—
Antwerp Blue and Crimson Lake	Red all gone	Gone blue	—
Indigo, Venetian Red, Yellow Ochre	Redder	Gone reddish	—
Prussian Blue, Yellow Ochre, Venetian Red	Redder	Gone red	—
Indigo, Raw and Burnt Sienna, Ind. Yellow	Browner	Gone brown	—
Indigo and Indian Red	Sl. redder	Red to 7	—

[1] The effects noted in this column took place after the pigments had been about one month in the dark.

Note.—Where numbers are given, the higher the number the deeper the tint referred to. Thus No. 1 is the faintest tint and No. 8 the deepest tint.

Note.—Sl. means slightly; V. sl. means very slightly; No. 1 is the faintest tint.

committee of water-colour artists, including the late Sir F. (Lord) Leighton, Sir E. J. Poynter (now P.R.A.), Sir Alma Tadema, Mr. Sidney Colvin and others, and that forty-six distinguished artists who used water colours furnished the authors with lists of the colours they were in the habit of using in their work.

The authors made a series of experiments with thirty-nine colours, in the first place, exposed to the full action of air and daylight. "The colours to be tested were applied by a practised hand to the paper in a series of washes. . . . In most cases as many as eight washes were applied, giving thus a complete series of eight tints." These strips were divided so as to give two equal strips each with the eight tints; these two strips were both placed in a glass tube open at each end and bent at the top, so that, while the complete action of air was ensured, the tubes, which were placed against a wall facing nearly south, were protected from the entrance of wet and dirt. One half of the tube was bound round with American cloth in order to protect one strip from the action of light. "The two pieces of identically tinted-coloured paper were therefore under exactly the same conditions in all respects, except that one was exposed to light and the other was in the dark." The papers were exposed from May, 1886, to March, 1888, and were observed on 14th August, 1886, in December, 1886, and in July and in November, 1887, and finally in March, 1888. It should be stated that a very careful approximation of the relative illuminating powers of bright sunlight, the light from the sky, and of diffused light from clouds was made, so that the authors were able, knowing the hours of sunshine at Kew and Greenwich Observatories during the period of their experiments, and taking the mean of these as representing the sunlight at Kensington, to state that between May and August, 1886, they considered that the pigments received a total illumination

equal to 2,225 hours of average blue sky. "This, of course, is only an approximate estimate." They also consider this to be equivalent to 100 years in a gallery illuminated similarly to those at Kensington. The results of the first and last examination of the tints are given in the preceding table (Table I. of the Report).

A second series of experiments was made in hermetically sealed tubes, with dried tinted paper and dry air. The results obtained are epitomised in the following table (Table III. of the Report) :—

Name of Colour.	Dry Air.
Carmine	Faded to 7
Crimson Lake	Gone to 5
Scarlet Lake	Faded and darkened
Vermilion	Gone black
Rose Madder	No change
Madder Lake	No change
Indian Red	No change
Venetian Red	No change
Brown Madder	Faded to 4
Burnt Sienna	No change
Gamboge	Faded to 3
Aureolin	No change
Chrome Yellow	No change
Cadmium Yellow	No change
Yellow Ochre	No change
Naples Yellow	No change
Indian Yellow	Faded to 4
Raw Sienna	No change
Emerald Green	No change
Terra Verte	No change
Chrom. Oxide	No change
Olive Green	No change
Antwerp Blue	Faded to 3
Prussian Blue	Faded to 5
Indigo Blue	Faded to 7
Cobalt Blue	No change
French Blue	No change
Ultramarine Ash	No change
Leitche's Blue	Faded to 5
Permanent Blue	No change
Payne's Grey	No change
Violet Carmine	Faded and brown
Purple Carmine	Faded
Purple Madder	Faded to 4
Sepia	No change
Vandyke Brown	V. sl. faded
Burnt Umber	No change
Brown Pink	Faded to 4

Of thirty-seven colours exposed to the action of moist air, only the following ten withstood the action of light under this condition : Indian red, Venetian red, burnt sienna, yellow ochre, raw sienna, emerald green, terra verte, chromium oxide, cobalt, and ultramarine ash ; both Prussian blue and Antwerp blue were entirely destroyed. Of twenty-nine mixtures only two were unchanged—raw sienna and Venetian red, and cobalt and Indian red.

A further series was made in which the colour was exposed to the action of moist hydrogen, so as to obviate the action of oxygen. Of thirty-six colours "no less than twenty-two remained unchanged; even carmine and crimson lake did not alter, neither did madder lake, Indian red, Venetian red, brown madder, burnt sienna, chrome yellow, yellow ochre, raw sienna, terra verte, chromium oxide, olive green, indigo, cobalt, French blue, ultramarine ash, permanent blue, Payne's grey, sepia, Vandyke brown, and burnt umber".

Thirty-nine experiments were made with single colours exposed in a (Sprengel) vacuum. "Violet carmine and purple carmine slightly darkened ; Prussian blue and purple madder and sepia slightly bleached ; but in all cases the action was very feeble. Twenty-four experiments were made with mixed colours, and the results are of much interest and importance. The mixtures containing Prussian blue changed, the other colours becoming dominant. Vermilion also blackened. With other mixtures hardly any change occurred."

The actions of the electric arc light, of heat without light, and of the light and products of combustion of coal gas were examined, and experiments were also made with body colours and with coloured light transmitted through red, green and blue glasses ; in this latter series colours exposed under blue glass were acted on to almost as great an extent as those under white glass, the difference being due to the opacity

of the blue glass. This fully confirms expectations based on theoretical considerations that the blue rays, from their greater oscillation frequencies approximating to those of the constituent atoms of substances, cause more decomposition than rays nearer the red end of the spectrum.

The conclusions arrived at by Dr. Russell and Captain Abney from these experiments are that—

"Mineral colours are far more stable than vegetable colours, and amongst those colours which have remained unaltered, or have only very slightly changed after an exposure to light of extreme severity, a good gamut is available to the water-colour artist. . . .

"The presence of moisture and oxygen is in most cases essential for a change to be effected even in the vegetable colours. . . . It may be said that every pigment is permanent when exposed to light *in vacuo*. . . .

"The effect of light on a mixture of colours which have no direct chemical action on one another is that the unstable colour disappears and leaves the stable colour unaltered appreciably.

"Our experiments also show that the rays which produce by far the greatest change in a pigment are the blue and violet components of white light, and that these, for equal illumination, predominate in light from the sky, whilst they are less in sunlight and in diffused cloud light, and are present in comparatively small proportion in the artificial lights usually employed in lighting a room or gallery. The experiments have also shown that about a century of exposure would have to be given to water-colour drawings in galleries lighted as are those at South Kensington before any marked deterioration would be visible in them, if painted with any but the more fugitive colours; and that when the illumination is of the same quality as that of gaslight, or of the electric glow light rendered normally incandescent, and

of the same intensity as that employed in those galleries, an exposure to be reckoned by thousands of years would have to be given to produce the same results. We have not taken into account the action, if any, which might arise from the products of combustion where gaslight is the illuminant, and which our experiments so far have shown to have but a trifling effect, nor of any modification of hue which might be due to change in the whiteness of the paper on which the paintings were made, but simply to the change in the colours themselves."

A suggestion as to the use of yellowish glass in galleries is also made in this report.

(B) Decorative Uses.

Under this heading we must include all those applications of pigments in which the suitable adornment of useful or quasi-useful objects is the principal purpose to be served, considerations of pictorial accuracy or effect or of protection of surface being subordinated to this in a greater or less degree, according to the peculiar circumstances of the case. These applications would comprise all kinds of mural decoration, including coloured-glass windows, the adornment of keramic ware of all kinds, of glass and of indoor (to a certain extent of outdoor) woodwork, and in some cases of metal work; the media employed in these cases are, of course, most varied in their nature.

The requirements of pigments to be used for decorative purposes are, naturally, somewhat allied to those of the artist on the one hand, and to those of the strict utilitarian on the other. A choice—not so great as the artist demands, for the decorator's depictive efforts are more conventional than imitative—of colours is obviously needful, as is also permanence of rather a different kind to that to which the artist endeavours to attain. The conditions under which decoration is employed

are usually more trying, both as regards atmospheric and other influences, because decoration is, after all, necessarily subordinate to human comfort and convenience. A painted ceiling, however lovely, is the top part of a room which should serve a useful purpose; a beautiful vase, however useless, is the descendant, though perhaps very remote, of a jar used to hold water, corn, or wine, or oil, or some other of the possessions of early communities, and still in many ways approximates to these more useful members of its family; a stained-glass window should be a means of letting in light and keeping out rain and wind from a building; a painted panel of a door or cabinet is primarily part of a structure, and though in many cases these things have been used by the artist as means by which he can exercise the pictorial art, they cannot be considered as the most suitable. The kind of permanence, therefore, required is rather of surface than of tint. A colour which will adhere well to the material and allow of the surface being cleaned, will, if it retain its tint fairly well, be preferable to one which, retaining its tint better, is more susceptible to atmospheric influences or wear.

It must be borne in mind that, whereas the pictorial artist subordinates his surface and methods to his subject, choosing the most suitable surface and medium, he who seeks to excel in decoration must adapt everything to the surface or thing to be decorated; the colours, the medium, must be such as on a certain object will produce the best *effect* and most enduring. The question of cost is also, considering the often extensive nature of such work, one which must not be neglected; also a due sense of proportion must be exercised in deciding to what extent perfection and permanence are likely to be required, or elaborate and costly schemes justified.

As the suitability of pigments for this class of work so much depends on the nature of the surface to be decorated

and the consequent colour-vehicle to be employed, it will be more convenient to consider the matter under the heading of methods employed in applying pigments rather than in this place; it always being remembered that the perfection to be sought in this sort of work is not of that absolute kind which is always desirable for serious artistic work, except in the very highest kind of decoration, which, in our opinion, is only legitimate in those cases where the permanence and proper treatment and receptive condition of the building or structure to be decorated can be well guaranteed. A painted ceiling, which is quite legitimate at Hampton Court or Greenwich, where the conditions are favourable, might be prepared and executed with much more costly and carefully selected pigments, media and surface than would be justifiable in a private house, which is liable to demolition for local improvements, or to premature senile decay. (What is true of materials is still more true of the worker !)

(c) Protective Uses.

From the purely utilitarian point of view these are the most important uses to which pigments may be put. The principal materials treated with paint for this purpose are wood and iron, and such treatment in each case becomes necessary only when exposure to moist or otherwise specially active air, or to water, is liable to cause deterioration of the surface with its subsequent general decay; and in the case of wood when it affords an easily cleaned surface. So far as we know, wood or iron exposed to perfectly dry air would be unaltered for an infinitely long period, but as this cannot be the case with articles in common use, or exposed to the weather, or immersed in water, the use of paint or varnish must be resorted to in all work that is intended to be of a permanent character, except, perhaps, in the case of very hard woods, which often have very high weathering qualities.

The object of painting or varnishing iron- or wood-work is, apart from considerations of appearance, to form a surface coating, impervious alike to air and water, which will prevent iron from rusting and wood from becoming waterlogged, swelling, and perhaps, on drying, cracking, and in course of time becoming rotten, water and air having no action, either direct or indirect, on the surface.[1] This coating in many cases, as ships' sides and iron- and wood-work and all work which must be handled much, must be not only impervious but tough, and not easily rubbed off, and in all cases must be fairly permanent, so that renewal is not frequently necessary; this is especially the case in large engineering work, where the difficulty of getting at the parts of a structure is often great.

Protective applications for such work may be considered under the following groups :—

(1) Asphaltic varnishes.
(2) Oil varnishes.
(3) Paints.
    (*a*) Presumably inert to the medium in which used.
    (*b*) Active in forming a varnish with the medium.
    (*c*) Antifouling by reason of their own erosion.

Concerning the relative value of members of the above groups opinions vary greatly, and, unfortunately, in this, as in many other cases, opinion has been allowed to take the place of definitely ascertained facts : a certain coating has

[1] It seems probable that many substances are less protective than might, at first, be expected when applied to metal-work, owing to one or both of the following reasons : (*a*) small quantities of soluble salts are through faulty preparation contained in the pigment which may either act directly on the surface in the presence of moisture, or which may absorb water and, producing minute crystals of different volume and form from the original salt, tend to weaken the coating by mechanical action; (*b*) the pigment may contain constituents which are decidedly electro-negative to the metal coated, and so set up electro-chemical action with erosion of that metal.

done well under one set of conditions, and is therefore considered by its user as the protective coating *par excellence*, while another coating, under totally different conditions, is found by another individual to be satisfactory, and he is of opinion that *this* is the material to be used in all cases. Some attempts have, however, been made from time to time by chemists and engineers to attack the problem of protection of iron-work from some other standpoint than the mere weathering of some isolated iron structure, possibly under abnormal conditions. A paper, in which most of the work done in this direction is examined and discussed, and a new series of valuable experiments described, was read by Mr. Harry Smith, F.I.C., before the Newcastle Section of the Society of Chemical Industry in December, 1899.

It would appear from this paper that most writers on the subject agree (1) that the work to be treated should be as clean and free from scale as possible; this to begin with ensures the absence of any particles much more electro-negative than iron; (2) that a treatment with hot (or cold) linseed or boiled linseed oil is desirable both as a protective coating and for the paint to adhere to more firmly than it will to the untreated iron (Mr. Smith's and some other experiments do not show this). Beyond these two points there is very little agreement on the part of the various experimenters, as the following quotations will show :—

Iron oxide paints adhere better to ironwork than lead paints. Asphaltum paints are not satisfactory.

E. Gesler.

The red paint known as oxide of iron, and which was claimed to be a rust preventative, possesses no inherent quality of that kind.

Engineer.

Iron oxide paints should not be used on iron, as the pigments themselves act as carriers of iron and produce rusting.

A. H. Sabin.

Toltze obtained the best results with genuine asphalte varnishes.

The method of experimenting adopted by Max Toltze, and

later by Mr. Smith himself in his second series of experiments, was as follows (Toltze's description) :—

"The iron dishes were about twelve inches in diameter and about half an inch deep, having a capacity of about half a pint. The scale or skin was carefully removed before painting, so as to have a clean surface of iron exposed to the paint. Two dishes were painted with each kind of paint, one of them receiving one coat, the other two coats, the first coat having dried thoroughly (for at least a week) before the second coat was applied. After the second coat had completely dried and hardened these dishes were exposed to the so-called water-and-moisture test, in which a given amount of water is placed in the dishes and allowed to evaporate to dryness at the ordinary temperature of the room. This is repeated a number of times until the inside of the dishes begins to show more or less rust. All dishes were carefully examined before each refilling. After most of the water has evaporated there remains at the junction round the edge a thin film of water, which, in contact with the carbonic and other acids in the air, acts on the paint in such a way that the iron under the paint begins to rust. The rust thus formed develops more and more after each evaporation, in some cases practically covering the whole dish in a short period."

Mr. Smith carried out experiments with forty-nine different preparations under the conditions described hereunder by himself :—

"The tests were carried out in three different ways :—

"1. By painting shallow iron dishes and exposing them to the action of slowly evaporating water as described in Mr. Toltze's experiments quoted above.

"2. By exposing a set of painted iron plates to the continuous action of the weather for a period of twelve months; and

"3. By exposing painted iron plates to the continuous

action of water in a similar manner to the tests made by Mr. Thomson and myself in 1894.

"1. The paints employed were prepared by grinding the pigments with linseed oil on granite rollers to a stiff paste in the proportions given below; these were thinned to the consistency of ordinary paint with boiled linseed oil of the best quality, and capable itself of yielding a dry film on a glass plate in about seven hours under ordinary conditions of temperature, etc.

"Each plate or dish was given two coats of paint, the second being applied after the first had become thoroughly dry; the tests were commenced when the second coats all appeared to be dry and firm.

"Let us take the dishes first. Each dish was about five inches wide by half an inch deep, and was filled with ordinary town water; they were placed side by side upon a table, and were not touched during the three months over which the trial extended; but as soon as the water had completely evaporated from each dish it was immediately refilled with fresh water. During the three months each dish dried and was refilled six times.

"In most cases all traces of paint have disappeared, and there is present a thick deposit of rust mixed with the suspended and soluble impurities present in the evaporated water.

"The dishes painted with the following paints are practically unaffected, and have withstood the very severe conditions of the trial:—

Red lead paint 'A' Red lead paint 'B' " " " Orange lead " Vermilionette " Scarlet red "	Practically unaffected.

"The following are slightly rust-stained, and are placed in order of merit.

Zinc white (oxide) paint		Slightly rust-stained; placed in order of merit.
'A' Zinc white	"	
'C' " "	"	
Lithopone	"	
White lead	"	
'A' " "	"	
'C' " "	"	

"As to the thirty-six other paints tried in this way, all appear to have suffered equally; but it was noticed that the dish painted with boiled linseed oil simply was the first to show deterioration, and has apparently produced the greatest amount of rust.

"2. The forty-nine iron plates, which were painted and exposed to weather for twelve months, all stood this test remarkably well, showing that all the paints were of fairly good quality under moderate conditions.

"There was one exception, however; the plate which received two coats of boiled oil speedily became spotted with rust, and at the end of the year was much corroded. All the painted plates became very much darker in colour owing to the deposit of soot from the air, but most of this I have since removed by rinsing the plates under the water-tap.

"3. In these experiments I painted strips of sheet-iron as before; and when the second coats were all dry and hard each plate was placed in a wide-mouthed glass bottle, and the same volume of ordinary tap water was added in each case. The bottles were then placed on a shelf immediately below the laboratory bench, so that the open mouths of the bottles were about one-eighth of an inch from the under side of the table; in this way the entrance of dust was almost entirely prevented, and evaporation was greatly checked, but there was access of air to the interior of each bottle.

"In this third series the tests were made in duplicate for

the sake of greater accuracy; the figures given below in the third column are the mean of two results, and the duplicates agreed very closely with each other in almost all cases.

"The bottles were now allowed to remain untouched for three months. After about seven days several of the plates were perceptibly affected; this was shown by a turbidity in the water; as oxidation proceeded a red precipitate of ferric oxide, or rust, appeared and slowly subsided to the bottoms of the bottles. After three months' exposure the plates were removed, and the amount of iron present in the liquid, and the deposit of rust in each bottle, were determined by analysis, and the total amounts of ferric oxide obtained in each case were calculated to pounds weight of rust per 1,500 square feet of painted iron surface; but, of course, this is rather under than over the total amount of corrosion, as a certain quantity of corroded iron was loosely attached to each plate and to the film of paint. The results obtained, and the composition of the paint in each case, are shown in the following table, and it must be understood that these paints are the same as those employed (1) on the shallow iron dishes, and (2) on the plates which were exposed to the weather for twelve months:—

Paint.	Composition.	Rust from 1,500 Sq. Yards.
Red Lead—	Per Cent.	Lb.
Red Lead	88·88	None
Raw Linseed Oil	11·12	
'A' Red Lead—		
Red Lead	45·00	None
Barytes	45·00	
Raw Linseed Oil	10·00	
'B' Red Lead—		
Red Lead	22·00	None
Barytes	66·00	
Raw Linseed Oil	12·00	
Orange Lead—		
Orange Lead	88·88	None
Raw Linseed Oil	11·12	
Vermilionette[1]—		
Barytes	33·33	None
Vermilionette	58·80	
Raw Linseed Oil	7·87	
Scarlet Red[2]—		
Scarlet Red	88·88	None
Raw Linseed Oil	11·12	
Pure Zinc White—		
Zinc White (Zinc Oxide)	87·30	Traces
Refined Linseed Oil	12·70	
'A' Zinc White—		
Zinc White	45·00	Traces
Barytes	45·00	
Refined Linseed Oil	10·00	
'C' Zinc White—		
Zinc White	27·27	Traces
Barytes	63·63	
Refined Linseed Oil	9·10	
White Lead—		
White Lead	92·56	75
Refined Linseed Oil	7·44	
'A' White Lead—		
White Lead	53·78	80
Barytes	40·33	
Refined Linseed Oil	5·80	
Pale Oxide—		
Pale Oxide (about 52 per cent. Fe_2O_3)	83·60	81
Boiled Linseed Oil	16·40	
Lithopone—		
Lithopone (Zinc Sulphide, Zinc Oxide, Barium Sulphate)	87·50	90
Refined Linseed Oil	12·50	
'C' White Lead—		
White Lead	50·52	95
Barytes	42·10	
Refined Linseed Oil	7·38	

[1] 'Vermilionette' is a pigment composed of Orange Lead on which has been precipitated about 10 per cent of Eosine.

[2] 'Scarlet Red' is Red Lead on which has been precipitated Aniline Scarlet.

Paint.	Composition.	Rust from 1,500 Sq. Yards.
	Per Cent.	Lb.
'A' Red—		
Barytes and Calcium Carbonate	78·80	118
Ferric Oxide (95 per cent. Fe_2O_3)	8·47	
Raw Linseed Oil	12·73	
'C' Red—		
Barytes	80·57	123
Ferric Oxide (95 per cent. Fe_2O_3)	7·55	
Raw Linseed Oil	11·88	
Deep Oxide—		
Ferric Oxide (96 per cent. Fe_2O_3)	86·89	123
Raw Linseed Oil	13·11	
Middle Oxide—		
Ferric Oxide (94 per cent. Fe_2O_3)	86·89	134
Raw Linseed Oil	13·11	
Extra Bright Oxide—		
Ferric Oxide (90 per cent. Fe_2O_3)	82·35	137
Boiled Linseed Oil	17·65	
Barytes—		
Barytes (Natural Barium Sulphate)	88·00	155
Raw Linseed Oil	12·00	
Pure Oxide 'C'—		
Ferric Oxide (90 per cent. Fe_2O_3)	76·30	160
Boiled Linseed Oil	23·70	
'C' Celestial Blue—		
Barytes and Calcium Carbonate	78·04	160
Celestial Blue (a form of Prussian Blue)	9·74	
Raw Linseed Oil	12·22	
'B' Prussian Blue—		
Prussian Blue	22·76	168
Barytes	45·52	
Raw Linseed Oil	31·72	
Pure Middle Chrome Yellow—		
Middle Chrome Yellow	83·58	177
Raw Linseed Oil	16·42	
Pure Raw Sienna—		
Raw Sienna	74·66	197
Raw Linseed Oil	25·34	
Pure Graphite—		
Graphite	69·56	215
Raw Linseed Oil	30·44	
Pure Prussian Blue—		
Prussian Blue	48·27	221
Raw Linseed Oil	51·73	
Pure Indian Red—		
Indian Red (70 per cent. Fe_2O_3)	82·35	227
Raw Linseed Oil	17·65	
'A' Vandyke Brown—		
Barytes	56·00	230
Raw Linseed Oil	13·33	
	30·67	
'B' Middle Oxide—		
Barytes	76·22	244
Oxide of Iron	12·30	
Raw Linseed Oil	11·48	

Paint.	Composition.	Rust from 1,500 Sq. Yards.
	Per Cent.	Lb.
Ivory Black—		
Drop Black (Charcoal Black)	60·00	250
Boiled Oil	40·00	
Turkey Red—		
Turkey Red (95 per cent. Fe_2O_3)	81·16	262
Raw Linseed Oil	18·84	
'A' Celestial Blue—		
Barytes and Calcium Carbonate	80·56	266
Celestial Blue	11·83	
Raw Linseed Oil	7·61	
'B' Chinese Blue—		
Chinese Blue (another form of Prussian Blue)	22·76	275
Barytes	45·52	
Raw Linseed Oil	31·72	
'A' Italian Ochre Paint—		
Italian Ochre	38·74	296
Barytes	19·00	
Raw Linseed Oil	42·26	
'A' Middle Brunswick Green[1]—		
Barytes and Calcium Carbonate	69·99	309
Superior Middle Brunswick Green	18·24	
Raw Linseed Oil	11·77	
'C' Middle Green—		
Barytes	78·32	322
Superior Brunswick Green	9·79	
Raw Linseed Oil	11·89	
Superior Yellow—		
Barytes and Calcium Carbonate	63·07	326
Chromate of Lead	22·51	
Umber	3·31	
Raw Linseed Oil	11·11	
English Umber—		
English Umber	57·51	336
Raw Linseed Oil	42·49	
'A' Black—		
Barytes and Calcium Carbonate	68·99	352
Carbon Black	8·42	
Manganese Dioxide	2·46	
Boiled Linseed Oil	20·13	
Burnt Turkey Umber—		
Burnt Turkey Umber	59·20	353
Raw Linseed Oil	40·80	
'C' Yellow—		
Barytes and Calcium Carbonate	79·28	369
Chromate of Lead	8·31	
Raw Umber	1·72	
Raw Linseed Oil	10·69	
'C' Black—		
Barytes and Calcium Carbonate	79·30	392
Carbon Black	4·35	
Manganese Dioxide	1·30	
Raw Linseed Oil	15·05	

[1] A mixture of Lead Chromate and Prussian Blue.

Paint.	Composition.	Rust from 1,500 Sq. Yards.
Middle Purple Brown—	Per Cent.	Lb.
Barytes and Calcium Carbonate	65·52	398
Oxide of Iron	27·03	
Raw Linseed Oil	10·45	
'A' Ultramarine—		
Ultramarine	52·63	425
Barytes	26·32	
Raw Linseed Oil	21·05	
Burnt Sienna—		
Burnt Sienna	56·00	439
Raw Linseed Oil	64·00	
Chinese Blue—		
Chinese Blue	48·27	441
Raw Linseed Oil	51·73	
Boiled Linseed Oil—		
Boiled Linseed Oil	—	500
Raw Turkey Umber—		
Raw Turkey Umber	51·85	510
Raw Linseed Oil	48·15	

"I think that these three series of experiments, carried out under such widely different conditions, and yet yielding such similar results, go to show that red or orange lead form the best basis for paint pigments amongst those which are in every-day use for iron work, especially in situations where excessive moisture is likely to be met with.

"At the same time it must be said that, owing to the vigorous chemical action set up in such paints, it is necessary that the mixing process shall immediately precede the actual painting.

"Red-lead paints have not quite the same degree of firmness as a good oxide of iron paint, which will withstand a great amount of rough usage when once it is perfectly dry, and this tough and elastic coating yielded by genuine oxide of iron paints has much to do with their undoubted popularity for outdoor work; the colour also is far more pleasing to the eye than the crude, harsh tone possessed by red lead paints.

"Zinc oxide appears to have a very high protective value as a pigment for use on iron, and stands better in this respect

than white lead; also, zinc-white paint, when pure, has a good body and covering power, and has the great advantage of being non-poisonous to the workers.

"In a somewhat similar, but less severe, series of trials made in 1897, I got a better result with graphite paint than in these experiments. A pure graphite paint was used and the result showed more corrosion than with pure zinc-oxide paint, but less corrosion than with pure oxide of iron paint; red-lead paints in these experiments also gave the best results, and still show no rust after two years' immersion.

"It is interesting to note the effect produced by the inert pigments, barytes and Paris white. I believe the best treatment for iron structures is to give them one or two coats of genuine red-lead paint—freshly ground; and I would follow this up with at least two coats of either a genuine oxide of iron paint, or, in some cases, of zinc-white paint made from pure zinc oxide and genuine linseed oil."

These experiments of Mr. Smith's are extremely interesting and, as he says, certainly show very definitely the marked superiority of red lead and zinc white over most other pigments. White lead[1] occupies a high place on the list, as do most of the iron-oxide pigments. The amount of difference of action in the case of barytes and raw linseed oil and boiled linseed oil alone is remarkable; it is not easy to see why so inert a substance as barium sulphate should have any other than the merest mechanical action on oil; the difference is probably due to either the mechanical formation of a cement more impervious than a layer of oxidised oil alone, or to raw oil drying more slowly than boiled oil, forming a tougher coating less liable to crack and allow erosion to commence. The differences between Prussian blue alone and diluted with barytes, and Chinese blue alone and

[1] Mr. Smith in a private communication to one of us describes the white lead as made by the Dutch process.

similarly diluted, in each case with raw oil, suggest that the Chinese blue was not washed very free from alkaline salts in its preparation, or possibly contained traces of free acid or bleaching powder, which is sometimes used for oxidation. Some other differences, as those between raw and burnt sienna, are very remarkable, and in our opinion, having regard to the fact that "the duplicates agreed very closely with each other in almost all cases," the question of soluble impurity will be found to have a very important bearing on the preservative powers of pigments.

It is worthy of note that the materials which stand highest on Mr. Smith's list, the red and orange lead, zinc white and white lead, are all likely to have a considerable chemical action on oil, red lead having probably both an oxidising and hydrolysing action, and zinc white and white lead both being likely substances to saponify linseed oil, in each case of course only to a very slight extent. The inferiority of pure carbonate of lead to ordinary white lead (a mixture of carbonate and hydroxide) is well known. The following remarks of Prof. Church illustrate this: "I tried comparative experiments with . . . pure lead carbonate and the Dutch-made lead hydrated carbonate, or ordinary flake white. The two lead pigments were washed thoroughly with distilled water, and dried before being ground in linseed oil. The oil-paints thus prepared were spread in duplicate series upon glass, paper and primed canvas. One set was kept in a dark box; the other was exposed to strong light. So decided was the superiority of the ordinary flake white over the pure carbonate, when both series of specimens were examined after the lapse of various intervals of time, that I was reluctantly compelled to abandon my recommendation of the latter. Ease in working, solidity of body and rapidity of drying were not the only points of superiority, for the films of paint, after having been kept a year, showed differences

in hardness and in smoothness of surface, which were all in favour of the hydrated carbonate. No discoloration was observed in the specimens exposed to light, except in the case of the pair upon paper; the absorbent ground had withdrawn some of the protecting oil, and both specimens had equally darkened. In darkness all the specimens had become of a somewhat greyish yellow, the discoloration being about equal in all the pairs, the pair spread on paper having, as in the previous case, become darker than the others." [1]

II.—METHODS OF APPLICATION OF PIGMENTS.

In the following table the authors have included most of the better-known methods of applying colours to recipient surfaces, and have indicated for each method the medium used and the surfaces on which it can be suitably employed, together with the purposes, as distinguished in the preceding part of this chapter, for which the method is used, namely:—

(*a*) Artistic (depictive) uses.
(*b*) Decorative uses.
(*c*) Protective uses.

Method.	Medium.	Purposes Used for.	Surface on which Used.
Crayon, Pastel .	Chalk and Gum used solid	*a*	Prepared (usually backed) Paper
Water Colour .	Water with Gum, etc., and Glycerine	*a*	*Pure* sized Paper
Tempera . . .	Albuminous or Gelatinous Matter	*a*, *b*	Prepared Wood, Canvas, Plaster
Fresco (and Secco)	Lime Water, Baryta Water, Water Glass	*a*, *b*	Prepared Plaster
Encaustic . . .	Wax	*a*	Wood

[1] *Chemistry of Paints and Painting*, p. 271.

Method.	Medium.	Purposes Used for.	Surface on which Used,
Oil (or varnish) .	A drying oil, thinned	*a*, *b*, *c*	(*a*) Prepared Wood, Canvas, Copper; (*b* and *c*) almost all Surfaces
Keramic—			
1. Pastes . .	Clay	*b*	——
2. Glazes . .	A Glass	*b*, *c*	Porcelain or Earthenware
3. Majolica, Della Robia .	An Opaque Tin Enamel	*b*, *c*	Earthenware (an Opaque Enamel is also used on Glass)
4. Under Glaze 5. On Glaze .	Ground Coloured Glass Paste applied with Resinous Medium	*b*	Porcelain, Earthenware
Enamel. . . .	An easily fusible Glass or Frit	*a*, *b*, *c*	Metal (usually Copper for *a*)
Stained Glass .	Glass	*b*	——
Painted Glass .	An Organic Medium on Glass	*b*	Glass
Mosaic	——	*b*	Cement

Pastels and Crayons.

Crayons proper, as used for drawing, *e.g.*, the first sketch or outline of an oil painting, or for crayon studies, are usually of three colours—black, white and red. The black and red are used for outline and shading, the white to heighten lights.

The gradation of shade in crayon drawings may be made either in the same way as in pencil drawing, by hatching, or by rubbing the hatching lines together into uniform or graduated tints, resembling washes, either by the finger tips or by the use of a "stump"—a pointed roll of paper or leather.

Fine charcoal, such as is prepared by burning vine twigs, is frequently used as a black pigment for such drawings.

Coloured chalks, crayons or pastels are used in a similar manner, so far as the production of graduated or uniform tints is concerned, to the black and red chalks. Very beautiful soft effects may be produced by the use of soft pastels, and by employing a large number of these little crayons a great variety of tints are available, so that a fairly correct colour effect may be obtained.

Pastels are made of colouring materials diluted with a white base, which not only gives the required set of tints by the use of varying amounts, but brings the pigment into a suitably friable condition.

Each colour is made in a series of graduated tints, usually as many as six, from the fullest workable tint to quite a pale shade. When fine strokes with a tint not to be found in the set of colours are required, fragments of two or more pastels may be crushed under a "muller" on a glass plate, moistened, and then rolled up into small pastels between the fingers, and allowed to dry in the sun or before the fire. For such mixed tints on larger surfaces streaks of two or more pastels may be rubbed together by the finger in a homogeneous or graduated whole like a "wash" in water colour or a "softened" part of an oil painting.

One point about pastels to be remembered is that they are fragile; it is very easy to break them. The angles thus produced are extremely useful for giving fine touches, and the fragments can be made use of for rubbing in large surfaces of colour. In addition to these accidental sharp edges, the usual methods of cutting and grinding on glass paper may be adopted.

It is not possible by the use of such a method—the application of a diluted pigment to a white or only slightly tinted surface in isolated particles, not bound together by any dense medium causing much internal reflection—to obtain the rich full colours of an oil painting. Such drawings or paintings must, from the enormous amount of white light reflected, always have a weak unsaturated appearance, but for portraiture, especially female heads, certain kinds of landscape and flower painting, pastel drawing may be used with considerable success.

The following soft pastel crayons of French manufacture have been qualitatively examined by us:—

Colour.	Tint (1 is the deepest).	Apparent Specific Gravity.	Composition.	
			Pigment.	White Base.
A Rosy Scarlet	1	3·7	Eosin and Red Lead	Calcium Carbonate
	2	3·4		
	3	3·0		
	4	2.2		
	5	2·2		
Pale Brick Red	1	3·9	A Ferric Oxide pigment with Red Lead	Calcium Carbonate
	2	2·6		
Brownish Red	1	2·1	Do. do. do.	
	2	2·1	The amount of Red Lead greater in the lighter tints	——
	3	2·5		
	4	2·8		
Black to Whitish Grey	1	1·2	Bone or Ivory Black	Calcium Carbonate
	2	1·6		
	3	1·9		
	4	2·0		
Blue	1	1·7	Prussian Blue	Calcium Carbonate
	2	1·9		
	3	2·0		
	4	2·0		
	5	2·0		
Purple	1	1·05	Cochineal and Ultramarine	Calcium Carbonate
	2	1·5		
	3	1·9		
	4	2·0		
Yellow	1	2·7	Lead Chromate	Calcium Carbonate
	2	2·6		
	3	2·2		
	4	2·1		
Salmon Pink	1	3·6	Red Lead	Calcium Carbonate
	2	3·5		
	3	2·9		
Green	1	3·2	Brunswick Green (Prussian Blue & Chrome Yellow)	Calcium Carbonate
	2	3·3		
	3	2·8		
	4	2·3		
	5	2·1		
Crimson	1	1·5	A Carmine Lake	(1 Apparently undiluted Calcium Carbonate
	2	1·7		
	3	1·8		
	4	1·9		
Pale Reddish Brown	1	2·4	A Peroxide of Lead and Oxide of Iron	Calcium Carbonate
	2	2·1		
	3	2·2		
White	—	2·9	White Lead and Calcium Carbonate	
Brown Yellow (Ochre)	1	2·8	Ferric Hydroxide	White Lead
	2	3·5		
	3	2·5		Calcium Carbonate
	4	2·2		

The use of eosin in colours intended for permanent work is certainly not to be recommended. The other colours, with the exception of the violet and crimson, might reasonably be expected to be highly permanent except, in some cases, in a sulphuretted hydrogen atmosphere.

The determinations of the "apparent specific gravity" given in the above table are useful as indicating the relative proportions of colour and base, and were found very useful in directing the qualitative examination.[1]

The fullest crimson appeared to be an undiluted lake.

A quantitative analysis was made of the palest tint of blue, which had the following composition:—

Prussian blue	10·7
Calcium carbonate	78·0
Alumina	2·0
Other matters soluble in acid	0·6
Insoluble siliceous matter	8·7
	100·0

As the qualitative examination had indicated, the base was almost entirely carbonate of lime—probably a mixture of prepared chalk and china clay.

Water Colour.

This, in its generally recognised form, purely modern method of painting, in which our countrymen have so greatly excelled, is essentially a staining process. The colours, ground in water, with a suitable gummy medium are applied to the surface, a pure sized paper, in thin washes, the high lights being left uncovered, or only thinly washed with the appropriate colour; the darker parts are treated with denser washes, or two or more washes are applied until the desired colour is obtained. Very beautiful atmospheric effects are produced by this means, and good water-colour paintings have a light

[1] The apparent specific gravity of chalk ($CaCO_3$) as used for blackboard drawing is 1·30.

effect, which is not usually seen in oil paintings, owing to the reflected light containing a very much larger proportion of white light, as has been stated in the previous chapter. The rough surface paper often used contributes greatly to this result. It is not always that this peculiarity of water colour contributes to artistic effect. For interiors and most pictures where richness of colour is desirable oil is a more suitable medium. Nevertheless, a comparison of the tinted drawings of the early water colourists, pleasing as they are, with the more mature efforts of recognised masters, will show what can be done by this method in the way of colour imitation (not mere suggestion). There is one thing about water colour: it is impossible to reduce or paint out work which is too heavy, or requires other alteration. A method of obtaining small streaks of high lights, which seems to be regarded by masters as legitimate, is to scratch the already tinted surface of the paper with a knife, and so expose a fresh white surface.

Many modern works painted with colour ground in an aqueous medium are rather paintings in body colour than pure water colour. Of this type we may instance an imitation of one of the Chantry pictures (which may not be copied in oils), which was exposed for sale in London some few years ago. This, it is fair to state, was in avowed imitation of oils, but many works called water colours are painted more or less in this rather unsuitable manner—a sort of revival of tempera.

A report on the permanence of water colours by Dr. W. J. Russell and Captain Abney has already been alluded to at some length. Paintings by this method must of necessity be more susceptible to atmospheric influences than works in which the colour is imbedded in some protective material (as varnish) which, itself inert, more or less effectually precludes the access of moisture or air.

Tempera Painting.

This ancient method of painting appears to have been practised from very early times, but is not much used now for artistic purposes. That its capabilities were great is shown by the beautiful specimens we still possess of pictures painted by this method, which have not only retained all their beauty of colour, but in which effect has been obtained in a masterly manner. For artistic purposes, however, it is not difficult to see why it has been supplanted by the more convenient methods of oil and water-colour painting. Tempera, or distemper painting, is, to describe it briefly, water-colour painting in body colour. The surface employed was usually wood, sometimes linen stretched on wood, occasionally plaster. In the case of wood (or linen) the suitably smoothed surface was primed with whitening applied in a suitable aqueous medium (this prepared surface was called *gesso*) and the colours to be used in the picture applied in a similar medium to this surface when it had dried. The media of the early Byzantine school were very unsatisfactory in that they were far from colourless; honey, glue and such sticky substances were used by them, but Giotto, one of the early Florentines before alluded to in this chapter, appears to have introduced a less coloured medium, probably white of egg or white and yolk. With this more satisfactory medium, or with pale sizes and fish glues, tints could be prepared of much greater purity and more approximating to those obtained by the painters of classical antiquity. Considerable care must have been required in this method of painting to avoid, in applying colour to parts already partly painted, any stirring up of the former tint; it would seem that the application of washes to modify tint, as in water colour, or of glazing or painting over a surface with thin layers of transparent colour, as in oil painting, must have been extremely difficult with a method in which

the whole picture and the gesso could be washed off the surface. Be this as it may, the process in the hands of masters has proved most satisfactory, if it may be judged in the usual way, by its results; in fact, from some attempts made by ourselves we think the manipulative weaknesses of the method are more apparent than real.

The finished tempera painting being a very delicate and, for reasons discussed in the previous chapter, a somewhat weak and chalky-looking production, was treated in many cases with a coat of linseed oil or other varnish, which not only acted as a preservative, but imparted considerable brilliance to the picture.

From the standpoint of permanency, the principal objections to this method of working are: (1) the putrescible nature of the medium; (2) its hygroscopic nature, rendering the surface liable to considerable expansion and contraction in a moist atmosphere, and, therefore, to cracking and scaling; and (3) the chemical nature of the medium, which, containing sulphur, is likely on the least putrefaction to evolve sulphuretted hydrogen, and cause blackening of some mineral colours. All these objections are much reduced when varnish has been applied to the painting, as thus it is rendered less hygroscopic, and, consequently, less liable to any sort of chemical change, and is also rendered much more tough and tenacious. In the dry pure air of Italy tempera paintings have preserved their beauty for centuries, and it is to be hoped that, under glass in a gallery of fairly uniform temperature, those specimens which are in our public collections may, as things of beauty, be joys for ever!

Fresco (*Italian, Fresh*).

This favourite style of mural painting (for which it is particularly well adapted) is also a most ancient one, having been used by the Egyptians, Greeks and Romans. Anton

Mengs, an artist and writer of the eighteenth century, expressed his conviction, after having passed the winter of 1772-73 at Naples, that the mural paintings at Pompeii and Herculaneum were executed in the method "*buon fresco*". More recent scientific investigations confirm the correctness of this decision. These paintings, some 1,800 years old, having survived many vicissitudes, present abundant testimony to the permanence and suitability of this method for mural painting.

Buon fresco is so called in distinction from *secco*, a less satisfactory method of working; in the former method the painting is performed on the wet ground or *intonaco*, as it is called, in the latter the receptive surface is allowed to dry, hence the term *secco*.

The wall to be adorned in *fresco* should be dry and well built, and as far as may be free from vibration. It is first well damped with water, preferably free from any saline matter other than lime salts, and then the coarser plaster applied. This should consist of clean, sharp sand, mixed with pure lime[1] paste prepared by slaking lime from chalk,

[1] The following analyses of some Italian, Bavarian and English limestones which furnish a suitable lime for *buon fresco* may be of interest. They were undertaken by Mr. R. Phillips for Sir C. Eastlake.

Travertine.		Genoa.	
Carbonate of lime	99·4	Carbonate of lime	63
Alumina with a trace of oxide of iron	·6	Carbonate of magnesia	36
		Earthy matter, oxide of iron, Bituminous matter	1
	100·0		100

Brought down from Bavarian Alps by the Isar.		Durdham Down, Bristol.	
Carbonate of lime	80	Carbonate of lime	99·5
Carbonate of magnesia	20	Bituminous matter	·3
		Earthy matter	·2
	100		100·0

A limestone containing calcium sulphate should not be used for preparing lime for fresco.

good limestone or marble, with so much water as will form a creamy paste, and then allowing this to stand for, say, two months, loosely covered, in order that it may absorb carbon dioxide from the air and so become partially carbonated. According to Sir H. Davy's researches (confirming a statement of Vitruvius) on the paintings at Herculaneum and Pompeii, the ground used by the ancients was crushed marble cemented by lime paste. Pumice, asbestos fibre, infusorial earth, or any permanent binding substance, may be similarly used to impart firmness to the lime plaster. Each coat of this is allowed to set before another is applied, and is moistened in order to prepare it for the next coat. The final surface, or *intonaco*,[1] is laid on by the plasterer day by day, only so much being applied as can be painted over at a sitting. This final coat is, of course, laid very flat, and when it is set the outline of the design is marked off from a cartoon. The colours mixed with lime water or the lime paste are then applied; if they dry in too quickly that part of the surface should be sprayed with lime water, which will assist in binding them to the surface. Most careful precautions are necessary in *fresco* painting, both as to manipulation and the choice of colours; when these are duly observed the work is extremely permanent.

Owing to the alkaline nature of the medium the palette of the *fresco* painter is limited, and it is partly to this fact—only the most inert colours being admissible—that *fresco* paintings are so enduring. The following list of suitable colours may be of interest:—

[1] The Italians usually applied three coats: the *rizzaffato*, or rough coat; the *arriciato*, or sand coat; and the *intonaco*, or fine surface.

Red.	Yellow.	Green.	Blue.
"All kinds of Burnt Ochres" (H.) Burnt Sienna (H.) Oxides of Iron (H.) Lake-coloured Burnt Vitriol (H.) "All the Iron Reds" (C.) Some varieties of Vermilion (C.)	All kinds of Ochres (H.,C.) Raw Sienna (H.) Cadmium Yellow (C.) Cobalt Yellow (C.)	Terra Verte or Verona Green (H.) Cobalt Green (H.) Chrome Green (H.,C.) Guignet's Green (C.)	Ultramarine, real (H.); factitious (H.) Cobalt (H.) Some Ultramarine & Cobalts (C.)

(H.) Hess of Munich, an eminent fresco painter of the early nineteenth century.

(C.) Prof. Church.

Any colour which is altered by caustic alkalies, as Prussian blue, gamboge or chrome yellow, is unsuitable.

The chemistry of the process is tolerably obvious. The picture is painted on and becomes fixed in a ground of mixed lime and carbonate of lime, which, at the same time drying and absorbing carbon dioxide from the air, though mostly probably still containing free lime, becomes converted on the surface into a hard layer of calcium carbonate. This, being only to a very slight degree hygroscopic, and absolutely unacted on by any of the constituents of the air (carbon dioxide and water — a solution of carbonic acid — would slowly dissolve it, but this would only occur in the open air or in very badly constructed rooms), not only remains intact, but is, by suitable means, easily cleaned when exposure to a smoky or dust-laden atmosphere has impaired its pristine freshness.

Owing to the nature of the surface and the limited palette at his disposal, the works of the fresco painter have usually a somewhat sombre effect, this in London being usually heightened in a short time by a surface film of carbonaceous matter. Still, for important historical works and

mural decoration generally *buon fresco* is a most suitable process.

Vasari (*Lives of the Painters*) states of *buon fresco* that it is "truly the most virile, most sure, most resolute and durable of all modes".

Buon fresco, from its durable nature, possesses the advantage of being easily and safely cleaned. Bread, water and a sponge, wine (white?), and, it is said, vinegar[1] (!) may be used. Frescoes on unsuitable walls can also be transferred by glueing cloth to them and stripping off cloth and colour and re-transferring to another cloth. This apparently very heroic method has been used with considerable success; some transferred frescoes may be seen in our National Gallery.

Secco, or painting on an already dried but re-damped plaster ground, in colours mixed with lime water, is, as the picture is only on and not *in* the receptive surface, less suitable for serious artistic work; it was, however, to some extent used by the old masters.

Encaustic Painting.

This very ancient method of painting is chiefly of interest on account of its antiquity. From the very few details and very few specimens we possess of such work it would appear that colours mixed with wax were applied hot to the receptive surface—probably primed with a mixture of wax and white—on which the design had been traced with a point, and the colour masses were softened by local applications of heated tools. The method, though apparently eminently unsuitable for very artistic work, certainly had its advantages so far as permanence is concerned, as a comparison of the encaustic and the tempera painting brought by Mr. Flinders Petrie from Egypt will show.

[1] It seems obvious that any acid liquid is undesirable.

Oil-Colour Painting.

Though for decorative purposes colours ground in "drying" oils have been used from relatively early times, the adoption of an oil or varnish medium as a colour vehicle in artistic painting is usually attributed to the brothers Van Eyck, of whom it appears that the elder, Hubert, was born in 1366 and John or Jan in 1390; though the latter is more commonly credited with the discovery, it seems that Hubert was also a master of this development of the art, as a great part of their masterpiece (in oils), the "Adoration of the Lamb" at St. Bavon's, Ghent, is known to be painted by him. Be this as it may, it is certain that to these great brothers artists are greatly indebted, at any rate, for very great improvements in this method of painting, improvements which fitted it for the finest artistic work, as an examination of the picture "Jean Arnolfini and His Wife" by Jan will show. Of the Florentine painters Antonio Pollaiuolo was one of the first to adopt this medium. An example of this painter's work in oils is to be found in the National Gallery, "The Martyrdom of St. Sebastian" (No. 292).

The works of these early painters in oils, especially those of Van Eyck, were executed, it is evident, in a manner somewhat different to that practised by many modern artists. The three pictures by Van Eyck in the National Gallery (Nos. 186, 290 and 292) are remarkable for the flatness of the surface; they are all on panels, and though in the celebrated "Jean Arnolfini" (No. 186) some very clever effects, *e.g.*, the mirror, the chandelier and the crystal rosary, are produced, these are entirely due to colour, not at all to raised surface (of the put-on-with-a-palette-knife kind). On looking at the pictures very obliquely the differences in level of the outlines of objects are perceptible to a slight extent only. The surfaces in each case are covered with

minute cracks, especially where blackish brown (bitumen?) and green (Prof. Church suggests verdigris) have been used; there is also some evidence of a repair on the mirror in No. 186, but this looks more like the results of an accident than the effects of time. These pictures of Van Eyck were probably painted with a slower drying medium than oil and turpentine; perhaps a transparent balsam or gum resin entered largely into its composition. The exquisite finish is not, as Prof. Church well says, compatible with hurry. These pictures, No. 186 to a less extent than the others, have a rather highly varnished though not exactly shiny appearance, due probably to the peculiarity of the medium. The painting by Pollaiuoli is very large (9′ 6″ h. × 6′ 7½″ w.), is considered to be his most important and characteristic work and is painted in a much bolder style than Van Eyck's careful work; the colour surfaces are much more defined and the differences in level more noticeable; still there is no evidence of any attempt to obtain effect by loading parts of the surface with clots of colour; the differences in level are merely due to the use of different colours with different proportions of medium, and perhaps painted over more in some cases than others and consequently drying down differently. The blackish parts of this picture have become very blotchy and the whole picture is covered with minute cracks and some long ones, which latter have either not parted or have been satisfactorily repaired. The picture at close quarters presents a rather "sticky" appearance, due either to a varnishy medium or a liberal use of varnish after finishing: it is well preserved and still a fine bright picture.

Oil paintings are usually executed on prepared wooden panels or stretched canvas, in the case of less important pictures on prepared millboard, sometimes, as in the case of mural paintings after this method, on a prepared secco or dry plaster. Wood appears to have been the favourite surface

for small works in early times, and wood was particularly suitable to the delicate work of so many early masters. Panels should be of well-seasoned wood which has been cut up some time before it is finally planed and glass-papered, so that both back and front surface may be equally dry and seasoned. It is recommended by some ancient authorities that the wood should now be boiled. Prof. Church suggests soaking in water raised to 50° C., and then steaming; by this means soluble matters are extracted and albuminoids precipitated. When dry he recommends a wash on both sides of corrosive sublimate (we suppose very dilute—say 1-1,000) in methylated spirit. After this treatment, which renders it unfit for the growth of any organisms, the panel is dried in a warm-air chamber for some time, re-glass-papered and primed with white lead, copal varnish, and boiled oil (prepared in manganese salts, not lead). When this coat is quite dry another coat in the transverse direction is applied. Then coats of oil and white lead alone, and, finally, zinc white and drying oil. Each coat is allowed to dry hard, and is rubbed down with pumice powder before another is applied. Both sides should be treated alike to prevent warping owing to exposure of the back, but of course the rubbing with pumice stone is not necessary for the back. When compound panels were used by the old painters linen cloth, or less frequently parchment, vellum or tinfoil, was often stretched over them to receive the colour, and also, of course, the gesso or painting ground. Probably the use of a linen surface in this manner led to the now almost universal use of canvas stretched on a wooden wedged frame for oil painting. The following list of surfaces used for oil painting is compiled from the catalogue of the National Gallery:—

Panels.	Metal.	Textile.
Deal.	Copper (in many cases).	Canvas.
Oak.	Silver (1).	Linen.
Poplar.		Silk.
Beech.		Paper on canvas.
Chestnut.		

The oil usually used for grinding colours in is pure linseed oil; in the case of badly drying colours, "boiled" or other quick-drying linseed oil is used. The following oils are also used to some extent in artistic work, though for decorative and protective purposes the cheaper linseed oil is always used.

Callemantia oil.
Hemp-seed oil.
Walnut oil (this is used by artists as less liable to cracking than linseed).
Poppy-seed oil (this is used by artists as less liable to cracking than linseed).
Niger-seed oil.
Fir-seed oil (used for varnishes).
Japanese wood oil (used for varnishes).

Colours ground in oil are, without dilution of some kind, too stiff, and sometimes too deep coloured for use alone. It is, therefore, common to dilute the pigment with a suitable white "base" to the required shade, and to reduce to a workable consistency with some volatile liquid miscible with oil. This liquid is usually "oil" or "spirit" of turpentine, a tolerably pure mixture of terpenes, with only a small proportion of oxidised product (resin), but of late years various turpentine substitutes, mostly of the nature of petroleum spirit, have to some extent come into use. It is also customary with both artists and decorators to use to a greater or less extent materials known as "driers," or "megilp," which, containing compounds of lead or manganese as their active constituents, facilitate the oxidation and "drying" of the oily vehicle.

A surface having been covered with a coat of paint prepared as above, two actions at once begin. The turpentine or other volatile thinning material evaporates more or less rapidly, and while this is going on the oil, especially if drying materials have been added, or the colour itself or the white diluting material, has high drying properties, becomes more viscous, and a film of hardened oxidised oil forms with the colour imbedded in it. This film, unless too much driers has been used, is tough and durable, and in the space of twenty-four hours or more is sufficiently established for a second painting. This convenient property of oil colour is of the greatest value to the artist and to the house painter; it enables the former to obtain very fine effects by the superimposition of thin "glazes" of transparent colour, by "stippling" and various other artistic devices; it also enables him to make alterations, to heighten lights and to run different colours close to one another in one painting in a way which is impossible to the water colourist; the house painter on his priming or first coat of good tough full-bodied paint can apply further protective and final decorative coats, the latter in colours which could not themselves be used as priming on account of their poor covering power and opacity.

In mixing paint care should be taken that too much thinning material is not used on the one hand, or, on the other, an excess of oil. In the former case, the solid particles are likely not to remain properly in suspension in the mass while it is being applied, and the result is that, though flat, the coat is of uneven tint and also dries very dull and chalky-looking owing to insufficiency of oil, while an excess of oil renders the paint difficult to work, slow drying, or, rather, forming only a surface skin with "tacky" paint underneath, and altogether unsuitable either for painting over or for protective purposes. The aim should be to use pigment, oil and turps in such proportions that a smooth

layer of pigment, perfectly imbedded in a thoroughly dried and resinified layer of oil varnish, is the result. In the case of artistic work and frequently in decorative work any deficiency in this respect is repaired by an application to the properly dried work of one or more coats of good transparent copal or other varnish. This not only increases the durability of the work by firmly cementing the colour particles in filling in the interstices caused by shrinking of the oil film, but by its high refractive index causes much of the white light which would be reflected from the unvarnished picture to be lost by internal reflection, and so gives that full mellow appearance and purity of tint which one associates with a finished oil painting. In the case of decorative work varnishing not only adds to its appearance, but gives to the paint a much greater durability by reason of the waterproof nature of the varnish.

Keramic Art.

A very important use of colours is to decorate pottery, and for this purpose the colours must be very carefully selected and applied in a highly specialised manner. We can only most briefly touch on some of the most important processes by which keramic ware is decorated. In the first place it is obvious that, in view of the high temperature to which all pottery is exposed in manufacture, the only colours admissible are those which are purely inorganic in their nature and which are non-volatile, at least at a red heat. Colours may be used in the following ways:—

I.—Coloured pastes.

II.—Colours on the paste.

(*a*) Glazes or transparent coloured glasses.

(*b*) Enamels or opaque glasses.

(*c*) Underglaze colours.

(*d*) On glaze colours.

It will be seen from this classification that two principal methods are adopted: the use of a coloured paste, which of course is the same colour all through, and the application of surface colours. We will consider these methods briefly.

I.—Coloured Pastes.

All pastes containing fusible as well as plastic materials can be beautifully stained by the addition of suitable metallic oxides before firing. We give some proportions used in the following table:—

Colour.	Colouring Material.	Parts.	
Pale Blue	Oxide of Cobalt	5	Paste to make up 100 parts in each case.
Deep Blue	,, ,,	10	
Green	,, ,,	5	
	,, Chromium	10	
Blue Green	,, ,,	2·5	
	,, Cobalt	1·25	
	,, Zinc	1·25	
Bronze Green	Calcined Oxide of Nickel	5	
Brown	,, ,, Iron	15	
Yellow	Oxide of Titanium	10	
Black	,, Iron	7	
	,, Cobalt	3	

Such coloured pastes would be used for mosaic tiles and tesseræ, coloured porcelain, etc.

II.—Colours on the Paste.

(*a*) *Coloured Glazes.*—These are applied either by dipping or with a large camel-hair brush to the surface of the "biscuit" or unglazed pottery. These glazes are largely used for coloured glazed tiles and self-coloured ware generally. A French glaze given by Salvetat, *Dictionnaire des Arts et Manufactures*, is—

Red lead	2,000 parts
Flint	1,000 ,,
Borate of lime	500 ,,

coloured by 40 to 125 parts cobalt oxide for *blue*, 100 to 500

parts copper oxide (CuO) for *blue greens*, 70 to 200 parts ferric oxide for ivory to strong yellow, 70 to 125 parts oxide of manganese (Mn_3O_4) for madder- to purple-brown, etc. The mixture is coarsely ground, melted, poured out into water and ground fine. An English mixture, rather less fusible, is made from flint 100, China stone 90, red lead 360, borax 40 parts, coloured similarly to the above.

A very lovely turquoise blue frit used by the Egyptians and Assyrians was examined by Sir H. Davy, who found it to be a frit of soda, silica and cupric oxide in the proportions: carbonate of soda 15, silica 20, copper 3. Vitruvius says it was made by mixing copper filings, alkali and finely ground sand, making into balls with water and fusing in a glass furnace. Salvetat gives the following:—

Body.		Glaze (fritted).	
Silica	93·0	Sand	900
Alumina	4·0	Sodium bicarbonate	400
Lime	2·0	Chalk	100
Potash	0·5	Cupric oxide	135

(*b*) *Enamels.*—These semi-vitrified, opaque materials are really stanniferous glazes—glazes made opaque by reason of their containing oxide of tin. Majolica and *Della Robbia* wares were decorated with such enamels. A revival of this kind of decoration has set in during this century, but, judging from the precautions taken in the winter for protecting the celebrated majolica fountain of the 1851 Exhibition, now outside the Bethnal Green Museum, the majolica of to-day is not a very suitable material for outdoor work in a variable and damp climate. A few enamels by Deck are taken, as are most of the recipes in this section, from the article "Pottery," in Thorpe's *Dictionary of Applied Chemistry*, by Mr. W. Barton.

White, lead and tin ashes, 44; sand, 44; soda, 2; common salt, 8; red lead, 2.

Yellow, white as above, 91; oxide of antimony, 9.

Blue, white as above, 95; cobalt oxide, 5.
Green, white as above, 95; cupric oxide, 5.
Yellow-green, white as above, 94; cupric oxide, 4; antimoniate of lead, 2.
Violet, white as above, 96; manganese dioxide, 4.

(*c*) *Underglaze Colours.*—Colours used for painting on the biscuit, which is subsequently glazed, must, when mixed with their silicious base, be sufficiently infusible and insoluble in the glaze to remain under (and protected by) it, and not to run into it, and must also be of such a nature as to hold to the glaze and not cause it to chip or crack. Underglaze colouring is the most satisfactory way of applying colours locally to porcelain or other keramic ware which is intended for use. We give some mixtures (from the article referred to):—

Black.—Eight parts native chromate of iron, 3 parts of Mn_3O_4, 3 parts of CoO, 1 part of flint; calcined together strongly, and then ground fine.

Dark Blue.—Four parts of CoO, 1 part of flint, 1 part of chalk; ground together.

Azure Blue.—Sixty parts of ammonium alum, 3 parts of CoO; calcined strongly, then ground and washed thoroughly till free from traces of acid.

Blue-Green.—Twelve parts of borax, 12 parts of chalk, 12 parts of oxide of zinc, 24 parts of green oxide of chromium, 4 parts of oxide of cobalt; calcine well together and grind till fine.

Dark Brown.—Eight parts of native chromate of iron, 4 parts of oxide of zinc, 2 parts of oxide of iron; ground well together, calcined strongly and re-ground.

Red-Brown.—Six parts of precipitated chromate of iron, 20 parts of oxide of zinc, 3 parts of litharge; calcine together strongly, and then grind till fine.

Pink Colour.—One hundred parts oxide of tin, 34 parts chalk, 1 part oxide of chromium, 5 parts silica; mixed well together, calcined strongly and ground.

Yellow.—Three parts oxide of antimony, 6 parts red lead, 2 parts flint, 1 part oxide of tin ; calcined together and then ground.

In all these colours great importance is to be attached to the grinding of the ingredients before, and the colour after, calcining.

(*d*) *On Glaze Colours.*—These colours are really fusible glasses, which, when applied to the glazed surface of the article (usually painted or printed with a resinous medium or thick boiled oil) and raised to a red heat, adhere before the glaze itself is remelted. They are by no means entirely satisfactory ; unless the coefficients of expansion of glaze and colour are almost equal, the colour is liable to crack and splinter. Work done in this way is less brilliant-looking and less artistic than underglaze work, besides being less permanent.

These colours are divided into two classes, regular kiln colours and hard kiln colours, according to the temperature of firing, the latter requiring the higher temperature. The composition of several fluxes, both Continental and Staffordshire, are given in the article in Thorpe's *Dictionary*, as also are several colours, including, in addition to the colouring materials already mentioned, oxides of uranium (black and yellow), antimoniate of potash, purple of Cassius (finely divided reduced gold), silver and oxide of gold.

The above brief outline of the methods of colouring keramic ware, and of the preparation and nature of the colours available for this purpose, will serve to indicate to some extent the requirements and scope of this kind of work. It is unnecessary to dilate on the extreme permanence which may be expected of suitable colours suitably applied to such durable materials, especially when either diffused through the entire mass, or in or under the glaze or enamel.

Enamel.

This method of applying colours, though strictly including the various methods of glazing and painting on keramic ware, is, in its restricted sense, the decoration or protection of metals by means of a coating of glaze which may or may not be used as the surface for further decoration.

Enamel painting, a method but little practised by artists on account of its difficulties and uncertainties, is really painting on enamel; a metal plate, usually copper, in some cases gold, is annealed and then covered with white enamel powder on both sides, the powder being an easily fusible glass with stannic or arsenious oxide or calcium phosphate suspended in it. This is then fired, cooled, and the coat of enamel which is formed ground smooth, a further coat is then burnt on the face to be painted, and a more fusible transparent flux then burnt on and ground. The painting is done with powdered coloured "frits," or glasses, in suitable media, and each colour burnt in separately. It will be seen that most subjects would require several paintings and firings. When it is considered that each of these operations is likely to result in failure, either through an inappropriate shade being burnt in, for the colour is only properly developed by firing, or by cracking in cooling, which, in the case of a large plate, is a serious risk, it will be understood that the art is but little practised.

Cloisonné is a method of decorating copper and other metal vessels in which the design is traced on the metal, and the different parts which should take different colours separated by strips of metal, or wires, fastened to the surface (by brazing). The low level surfaces thus formed are filled with enamel, and the whole is then fired, and when cold the surface ground smooth. The colours are in this kind of work separated by metal bands, or fillets, which show, like

the leading of a painted window. Another method, *champ levé*, practised in Germany and at Limoges, a town celebrated for its enamel paintings on convex copper plates in grey and white on a blue ground, was to trace the design on copper and then cut away the parts to be enamelled with a graver, filling in these hollows, firing, and then grinding smooth. In this case, as in that of cloisonné, raised metal surfaces are visible and must be treated as part of the design.

Enamel is used largely now on iron for advertising purposes. Iron sheets enamelled blue and white or other colours have largely supplanted the poster for permanent advertisements and notices. The method of working is similar to that for copper.

In any case it is desirable that the coefficients of expansion of metal and enamel should be so adjusted by experiment as not to be very different. If this is not the case chipping off is likely to occur on cooling.

The colours used for enamel work are very similar to those described as being used for the decoration of keramic ware; a description of many of these is given in the section devoted to that branch of art.

Stained and Painted Glass.

Glass is, as is well known, a mixture of various silicates obtained by fusion and subsequent cooling, this process being conducted so (relatively) rapidly that crystallisation does not take place, and the resulting product is (usually) transparent.

Mixtures of the silicates of soda and lime, potash and lime and potash and lead are used for the production of coloured glass, the colour being imparted by the addition of small proportions of various metallic oxides. The student of chemistry in a very early period of his career is taught to form deductions as to the nature of substances from the

colour imparted by them to "borax beads". The borax "pastes" thus produced are used in the manufacture of artificial gems for theatrical and other purposes. Speaking generally, the oxides which impart a colour to borax impart a similar colour to glass. We give a list of substances used for colouring glass which will indicate the general composition of coloured glasses.

Blue glasses are produced, the lighter sky-blue colours, by the addition of 0·8 to 1·2 per cent. of cupric oxide (CuO); the deeper, more violet glasses, by the addition of oxide of cobalt (about 0·15 per cent.), or zaffre (0·35 to 0·4 per cent). A pale blue or blue-green glass is produced by partial oxidation of glass coloured by iron.

Amethyst coloured glass contains 2 to 2·5 per cent. of manganese-dioxide (pyrolusite), mixed with about twice that amount of nitre to prevent reduction to the manganous state. (This agrees with the behaviour of manganese in borax in the oxidising and reducing flames respectively.)

Yellow glasses are obtained in a variety of ways: by the addition of wood or of charcoal, in which case carbon appears to be the pigment; by the addition of sulphur (not to lead glass, as this would produce lead sulphide, which is black), in which case a yellow alkaline sulphide appears to be produced or with manganese dioxide and ferric oxide, or by antimoniate of lead (antimoniate of lead is used as a yellow pigment by artists under the name of Naples yellow). Uranic oxide also produces a fluorescent yellow glass, the appearance of which is pleasing and is well known, somewhat resembling that of an alkaline solution of fluorescein.

Orange-coloured glass is prepared by using manganese dioxide, and ferric oxide, the ferric oxide being slightly in excess.

Red glass is coloured by cuprous oxide, Cu_2O (rose copper), in which case great care must be taken to avoid

oxidation to cupric oxide with formation of a blue or green glass. Metallic iron (1 to 1·5 per cent.) and cupric oxide (about 1 per cent.) are added, and the mixture is melted and stirred with an iron rod. The glass is colourless when taken out of the crucible, but turns red on cooling. A more crimson glass is obtained by the use of gold, which is added to the sand of which the glass is to be made, in the form of chloride. Not more than 0·1 per cent. gold is used, and even less than this gives a fine rich ruby red. The colour, like that of the purple of Cassius is due to the presence of finely divided gold.

Green glass is obtained by using a mixture of oxide of iron and oxide of copper, with the addition of nitre to maintain these in the higher state of oxidation. Chromium oxide also produces a green, as does a mixture of antimonious oxide and cobalt. Bottle green is produced by ferrous oxide, iron being added as iron filings, and dissolved by the glass to a ferrous oxide.

Black glass is produced by the use of mixtures of oxides as cobalt, copper, iron or manganese, one of these being in sufficient excess to remain undissolved as dark particles.

The addition of sulphur (7 to 10 per cent.) by forming ferrous sulphide also produces a black glass. This is prepared in Bohemia, and is known as hyalithe.

White glass, opal or translucent glass is prepared either by the use of stannic oxide with lead oxide produced by heating the metals together; by arsenious oxide in a lead potash or lead potash lime glass, or by calcium phosphate, or by the use of fluorides as cryolite or, better, sodium fluoride.

Aventurine glass contains either finely divided cuprous oxide, or finely divided copper. It is, at any rate, a yellow glass full of sparkling red metallic-looking particles. It is prepared according to Hautefeuille from such mixtures as the following :—

Crystal 2,000, saltpetre 200, copper turnings 125, ferric oxide 60 parts.

Or,

Sand 1,500, chalk 357, anhydrous carbonate of soda 801, carbonate of potash 143, saltpetre 200, copper turnings 125 parts.

Or,

White soda glass 1,200, sand 600, carbonate of soda 650, saltpetre 200, copper turnings 125.

When the glass is liquid, 38 parts of iron filings rolled up in paper are thrown into the pot, and the mixture stirred with a red-hot iron. The glass becomes blood red, opaque, and full of small bubbles, the furnace draught is stopped, the pot covered, heaped with ashes and allowed to cool very slowly. Next day the crucible is broken, and aventurine found to have been produced. It is difficult to produce a good article, as the product is liable to become streaky, to contain bubbles, or the crystals may be too fine.

Chromium aventurine was discovered by Pelouze in 1865. It is produced by heating sand 250, carbonate of soda 100, calc spar 50, bichrome (bichromate presumably) 20 to 40 parts. The chromium oxide resulting on fusion is in greater amount than will dissolve to form a green glass, and this excess is suspended in the glass as brilliant green crystals.

Speaking generally, it is admitted by glass-makers themselves that the glass of to-day, though certainly very superior to that of the early and middle part of last century, is decidedly inferior to good old glass in richness of tint, and probably in weathering qualities.

Painted glass such as is seen in windows is produced by shading and burning in the shades on coloured glass. Briefly, the process is this: The design is drawn full size from the coloured sketch on white paper in black chalk, or (in France) in white on blue paper, the different colours being marked on the parts. The coloured glasses are then

selected, agreeing as nearly as possible with the brightest parts of the respective colours in the coloured sketch, and are cut to shape with a diamond, shaded first in water colour, then in oil with an oxide of iron paint, a little borax being used as a flux. In some cases actual painting with similar colours to those used for tinting glass is resorted to. The plates are then placed on shelves covered with powdered lime in a furnace, which is heated sufficiently to so soften them that the shading sinks in and becomes incorporated with the glass. Various methods of shading, as smudging, stippling, and hatching with lines are adopted ; pieces of high light are, where necessary, wiped out of the shading before it is burnt in, and in some cases flashed glass (coloured and colourless glass welded together) is etched locally with hydrofluoric acid until only the colourless glass is left. The process is difficult and complicated, and the above is only the crudest outline. Much modern glass seems to be too soft to withstand the erosive effect of town atmosphere.

Mosaic.

Mosaic is a method of decoration in which small coloured dice or tesseræ imbedded in cement are arranged to form a pattern or design. It is, provided the cement is good, an absolutely permanent kind of work, as the tesseræ are usually composed of natural-coloured stones, or of marbles, or of fired earthenware. Speaking generally it is rather a method of utilising coloured substances for decoration than of application of pigments in the ordinary sense of prepared pigments, and needs no more than a passing notice here, though as a method of decoration, especially under the trying conditions which prevail in modern towns, its importance is very great.

CHAPTER III.

INORGANIC PIGMENTS.

I.—WHITE PIGMENTS.

White Lead (*Synonyms—Cerussa Alba, Cremnitz White, Flake White*).

Of all white pigments this is the most widely used and most important; it is also one of those most frequently sophisticated, being sometimes adulterated, and frequently replaced by other lead whites. Its great covering power, ease of working with oil and permanence in that medium, combined with its good drying qualities, render it most suitable both for use alone and for diluting other (coloured) pigments.

It is, we believe, entirely correct to state that none of the many artificial white leads or other white compounds of lead possess to anything like the same extent the all-round good qualities of white lead which has been prepared according to the so-called Dutch or stack process; even in those cases in which the chemical composition of the white as shown by analysis is correct the physical condition does not appear to be so satisfactory. One objection brought against white lead (principally by those interested in other whites) is that it is more or less blackened by exposure to air contaminated with sulphuretted hydrogen. This impeachment, so far as it goes, is correct, but under ordinary conditions serious alteration does not occur, and, a fact often disregarded, white lead on

exposure to light and pure air recovers in course of time. Very old pictures in which white lead has been used often exhibit an ivory-like yellowness, owing probably to combination with the oil or varnish of the medium, but this yellow colour is seldom sufficient to spoil an effect, and usually is by no means unpleasant.

This property of white lead, of entering into combination with linseed oil, is a most valuable one, as to it is probably due in no small degree the toughness and imperviousness of the coat obtained. The experiments of a maker of whites, quoted by Mr. A. P. Laurie in his Cantor Lectures, in which strips of canvas were painted with various whites and allowed to flutter in the breeze, and in which it was found that, after wind and weather had caused all the other whites to peel and crack, the canvas painted with white lead was still well coated, are particularly interesting in this connection.

The most ancient and most satisfactory method of preparing white lead is the so-called Dutch process, or stack corrosion. In this, lead in the form of coils or gratings is stacked up over pots containing dilute acetic acid or vinegar and imbedded in fermenting horse dung or spent tan; several layers of pots are stacked one over the other in large brick chambers or sheds capable of holding several tons of lead. The temperature of the stack rises considerably as a result of the fermentation of the dung or tan, the temperature of the mass reaching from 140° F. to 150° F. according to circumstances. Acetic acid vapours and carbon-dioxide are evolved, which attack the surface of the lead in the presence of aqueous vapour, forming first a film of lead oxide which is gradually converted into basic acetate of lead. This, acted on by carbon-dioxide, becomes white lead and normal lead acetate. The normal acetate and fresh lead oxide re-form basic acetate, which is again decomposed and re-formed, the resulting compound at the end of some months, when the heating

effect has passed off and chemical action ceased, being the mixture or compound of lead hydroxide and carbonate known as white lead. This forms a thick crust on the surface of the, by this time, much corroded lead plates, etc. This is detached and ground and levigated in order to obtain the requisite degree of fineness. The percentage of lead converted depends on its state of aggregation and on the details of working; it varies from 50 to 70 per cent. Some makers prefer to cast the lead into rather thick coils, stars or gratings, as it is easier to detach the white lead when the percentage of corroded lead is low.

In England tan is usually used, in Holland dung, to produce the carbon dioxide and to cause the requisite increase in temperature; it is also more common in England to use dilute acetic acid from pyroligneous acid rather than vinegar, otherwise the processes in general use in the two countries are similar. This process of stack corrosion is extremely slow, the operation, as has been already stated, extending over several months, but the product is, for reasons which will be considered below, most satisfactory.

A process closely allied to the stack process, and which may be considered as a *bonâ-fide* method of preparing white lead, is that used in Germany, originally at Kremsnow, but to a greater extent at Klagenfurt. Thin sheets of lead are exposed in wooden boxes, heated artificially to about 85° C., and submitted to the vapours rising from a mixture of wine lees and vinegar spread on the bottom of the boxes. A modification of this process consists in suspending the sheets of lead in chests or chambers on the floors of which are placed vessels of acetic acid. Air and carbon-dioxide are passed into these chambers, and in either case the German method is more rapid than either English or Dutch. The product, however, is not so satisfactory.

The French or Clichy method is altogether different from

either of the above processes. It was devised by the well-known chemist, Thenard, and is one of the earliest of the many precipitation processes. Basic acetate of lead is formed by digesting litharge (PbO) with acetic acid of 1·056 specific gravity. The mixture is kept agitated by a mechanical device, and litharge added until the solution has a specific gravity of 1·145. The liquor is then run into a settling tank where any insoluble matters deposit, and the clear solution is transferred to a vessel where it is treated with carbon-dioxide prepared by heating a mixture of chalk and coke in a kiln; the kiln gases are drawn off by a fan and forced through a scrubber, and then through pipes into the precipitating tank. In about twelve or fourteen hours the conversion is as complete as is possible—that is, white lead and normal acetate are formed. The latter is pumped off and digested with litharge to re-form basic acetate, the first washings of the white lead being used again, as they also contain acetate. The white lead formed is carefully washed and ground. This process is in some respects very similar to the dry processes, but the product is not so satisfactory as a pigment.

In Milner's process a basic chloride of lead is produced by the interaction of litharge, salt and water. The mixture at the ordinary temperature becomes white and pasty; a considerable evolution of heat occurs, and the solution becomes alkaline owing to the formation of sodium hydroxide. The decomposition is usually effected in mills, and the proportions used are 1 of salt, 4 of litharge, and 16 of water. The agitation is continued for about three hours (if for a shorter period the mass is too pasty), and after this time the entire mass is creamy, and can be run out. The carbonation is effected in an iron lead-lined vessel with hemispherical ends, placed upright. At the top is an opening through which the basic chloride mixture is introduced, and another by means of which the pressure is regulated; an opening near the

bottom serves to draw off the white lead and samples which are examined from time to time during the conversion. The carbon-dioxide is, as in the French process, prepared from coke and chalk, and is scrubbed in coke water towers. When the action is complete a test sample is no longer alkaline, as all the chlorine of the chloride has combined with the sodium previously existing as hydroxide, forming common salt; and if shaken in a glass vessel the creamy homogeneous mass leaves a frosted appearance on the sides, and in a few minutes the white lead has separated out, leaving a clear liquid above, and branching patterns on the sides of the vessel which were coated. Any further addition of carbon-dioxide causes a deterioration in quality of the product, which becomes granular. The white thus obtained is washed free from salt, and though inferior to stack lead, is well suited for use as a paint.

Many other processes, as precipitation from a solution of basic nitrate by CO_2, action of CO_2, air and water on finely divided lead, action of CO_2 on a paste of litharge and lead acetate, have been suggested and made the subject of patents. So far, however, none of these have yielded so satisfactory a product as that obtained by the older processes, though in many cases closely approximating in chemical composition.

Whatever process may be adopted, if a product at all satisfactory be required, it is necessary that very pure lead, such as is prepared by the Pattinson or Rogan processes, or by a modification of the Parkes zinc process, should be used for the preparation of white lead, as the presence of even very small quantities of other metals is likely to affect the colour of the product. A slight pink tinge, which is sometimes observable in corrosions, is said to be due to the presence of a suboxide of lead; others attribute it to the presence of minute quantities of silver compounds. The tan also, either by touching or by liquid from it falling on the deposit, is likely to cause discoloration. It must be

remembered that basic acetate of lead is an extremely good substance for removing colouring matters from liquids, and that any drippings from boards used in stacking are likely to give up any trace of yellow or brown colour extracted from the wood to the "corrosion". A discoloration, if not serious, is sometimes corrected by the addition of a very minute quantity of Prussian blue, which gives a bluish tinge, and makes the white appear very pure in tone.

A most important objection to the stack process, or indeed to any dry process of preparing white lead, is the deleterious effect the very fine dust raised has on the human system. This is certainly a serious drawback, and one which has in the past called for protective legislation on behalf of the work-people, who, in too many instances, require much supervision to induce them to take needful precautions.

We give below in full the special rules prescribed under the Factory and Workshop Acts, 1878-91, for observance in white-lead works:—

"Duties of Occupiers.

"1. They shall provide respirators, overall suits and head coverings, to be worn by the persons employed in the departments enumerated below, under 'Duties of Persons Employed'.

"2. They shall take care that every stack is fitted with a standpipe, or movable hose, and an adequate supply of water, distributed by a very fine rose or watering can, for damping the white bed before stripping.

"3. They shall see that no female shall be employed without a certificate of fitness from a medical man, to be obtained within one week from the date of employment.

"4. They shall see that no person shall be re-employed after absence through illness without a certificate from a medical man.

"5. They shall provide overalls for females in all blue beds where the returns are used without being remelted, and overalls and head coverings for females in all other parts of the works except the casting shops.

"6. That the wearing of shoes and stockings be optional, but that no females shall be permitted to wear the same shoes and stockings in the works as they wear in going to and from the place of employment.

"7. They shall provide sufficient bath accommodation for all men and women employed.

"8. They shall provide dressing-rooms, a dining-room, lavatories, and a cloak-room in which the ordinary clothes of all workers are to be kept apart from their working clothes.

"9. They shall arrange for a weekly visit by a doctor, who shall examine every worker individually, and who shall enter the result of each examination in the proper register.

"10. They shall cause such a register to be kept, and shall have entered in it the date when each worker commences and leaves employment, and the date when each worker takes a bath.

"11. They shall cause every case of illness from lead poisoning to be reported both to H.M. Inspector of Factories for the district, and to the Certifying Surgeon.

"12. They shall cause each man or woman to take a bath at least once a week, and to wash in the lavatory before bathing.

"13. They shall deliver to the persons employed the articles of clothing which are required to be worn, and they shall see that they are put on. At the end of every day's work they shall collect and have thoroughly washed all those which have been used in the stoves, and those which have been used in other departments, once a week.

"14. They shall see that the general lavatory is thoroughly cleansed and supplied with clean towels after every meal.

LIBRARY OF THE UNIVERSITY

"15. They shall have the dressing-rooms, baths, and w.c.'s brushed and cleansed daily.

"16. They shall not allow the workers to leave any clothes in the dining-room, or their ordinary clothes in any work-room.

"17. They shall see that the supply of hot and cold water, soap, brushes, and towels is sufficient in the bath-room and lavatories.

"18. They shall see that there are kept in close proximity to the workers in each department washing conveniences and a sufficient supply of approved sanitary drink, and they shall cause the people to take it.

"19. They shall set apart, and cause to be entered in a notice affixed in each department, a period of at least ten minutes, in addition to the regular meal-times, for washing immediately before each meal-time, and also before the end of the day's work; and they shall see that it is observed.

"20. They shall see that at the doctor's weekly visit the proper entries are on each occasion made in the register.

"21. Upon any person complaining of being unwell, they shall with the least possible delay give an order upon the doctor; and upon any person desiring medicine, they shall give a dose of the prescribed medicine kept at the works.

"22. Managers, etc., shall report immediately to the firm any instance which comes under their notice of any worker neglecting the regulations hereinafter mentioned.

"23. They shall examine all persons going out of the works, and shall not allow them to leave unless they are properly cleansed from lead.

"Duties of Persons Employed.

"24. Each man or woman before commencing work in any of the following departments shall wear as follows, having received the same from the person in charge:—

"Blue beds—Every woman to wear an overall suit in all blue beds where the returns are used without being remelted.

"White beds—One overall suit and head covering. Women inside the white beds to wear respirators also, but the 'Carriers' not.

"Washing and crushing—One overall suit and head covering. 'Roller' women to wear respirators also.

"Grinding—One overall suit and head covering.

"Setting stoves—One overall suit and head covering.

"Drawing stoves—One overall suit, head covering, and respirator.

"Paint-mixing—One overall suit and respirator.

"25. Each man or woman working at any white bed, or in setting or drawing stoves, or in the washing and crushing, grinding, or paint-mixing departments, before going to breakfast, dinner, or home, or before entering the dining-room for any purpose whatever, must—

"Put off the overall suit, etc., and give the same to the person in charge, or leave it in the clothes room.

"Brush every particle of lead dust from his or her clothes.

"Thoroughly wash face and hands in the lavatory, and be particular that no dust remain underneath the finger-nails.

"If not wearing stockings and boots, thoroughly wash the feet.

"26. Each man or woman must bathe at least once a week, and must wash in the lavatory before bathing.

"27. Each man or woman must receive and drink, at such times as may be stated in a notice affixed in the factory, such sanitary drinks as may be prescribed in such notice.

"28. Every white bed must be adequately watered on removal of the boards, and all trays of corrosions shall be well saturated with water before passing through the rollers.

"29. No person shall smoke or use tobacco in any work-place, or room, or take food in any part of the works, except in the dining-room.

"30. No person may seek employment under an assumed name, or under any false pretence.

"Respirators—A good respirator is a cambric bag with or without a thin flexible wire made to fit over the nose.

"Sanitary drink suggested { Sulphate of magnesia, 2 oz. / Water, 1 gallon. / Essence of lemon, sufficient to flavour.

"Prescribed medicine.

"*The following Departments to be specially Ventilated.*

"(1) Washing and crushing.

"(2) Grinding in water.

"(3) Paint (grinding in oil).

"(4) Drawing stoves.

"R. E. Sprague Oram,
"H.M. Chief Inspector of Factories.

"Under Section 9, Factory Act, 1891, any person who is bound to observe any special rules, as well as the occupier, is liable to penalties for non-compliance with such special rules."

The composition of white lead varies somewhat, according to the method of preparation, as has been very frequently stated by different authorities. It may be represented by the general formula, $xPbCO_3\ yPb(OH)_2$, a hydrated basic carbonate of lead. Some samples approximate in composition to the normal carbonate; others contain a rather excessive amount of hydroxide. The general opinion as to the normal composi-

tion of this substance is that it contains two molecules of carbonate to one of hydroxide, $2PbCO_3Pb(OH)_2$. The excess of carbonate is usually supposed to be caused by the presence of free acetic acid towards the end of the process, as it would appear that it is only under such conditions that the normal carbonate forms, the product otherwise always being basic. A certain amount of normal acetate of lead is always present in unwashed white lead. One object of the washing is to remove this, but the amount is usually less in lead prepared by the English or Dutch processes than in that obtained by other methods, and it is in these two processes that the vinegar or pyroligneous acid is allowed to evaporate quite to dryness, and fermentation of the dung or tan to go on for a further period, during which CO_2 is evolved and most of the normal acetate converted into basic acetate, and then to basic carbonate.

We give in the following table the composition of several samples of genuine white lead ground in oil, the composition of the oil-free white being given in the lower part of the table, and also the approximate molecular proportions of carbonate and hydroxide :—

WHITE LEAD GROUND IN OIL.

	I.	II.	III.	IV.	V.	VI.
Oil, moisture, etc.	6·5	6·5	7·2	10·3	7·3	5·5
Lead carbonate .	71·3	64·0	66·3	66·5	67·0	65·4
Lead hydroxide .	22·2	29·1	25·2	23·2	25·7	28·7
Other matters .	—	·4	1·3	—	—	0·4
	100·0	100·0	100·0	100·0	100·0	100·0

DRY MATTER.

	I.	II.	III.	IV.	V.	VI.
Lead carbonate .	76·4	68·5	71·5	74·2	72·3	69·2
Lead hydroxide .	23·6	31·1	27·2	25·8	27·7	30·4
Other matters .	—	·4	1·3	—	—	0·4
	100·0	100·0	100·0	100·0	100·0	100·0
Molecular ratio—						
$Pb(OH)_2 : PbCO_3$	1 : 2·94	1 : 1·99	1 : 2·37	1 : 2·59	1 : 2·35	1 : 2·06

The foregoing figures may be taken as representing the composition of average samples of white lead prepared by dry corrosion. It will be seen that the molecular ratio, $PbCO_3:Pb(OH)_2$, varies from almost 3:1 to 2:1. Samples have been examined by various authorities in which the ratio was as high as 5:1, but these are evidently quite abnormal.

A sample of "flake white" sold for decorators' use in large tubes had the following decidedly abnormal composition :—

Oil-Free Matter.

Lead carbonate	94·1
Lead hydroxide	3·3
Calcium carbonate, etc.	2·2
Fatty acids from lead soap	0·4
	100·0

It was ground with 9 per cent. of oil.

We have examined samples in which the ratio,

$$PbCO_3:Pb(OH)_2,$$

was very much lower than 2:1, but it is probable that none of these were stack-corroded. Some, we know, were prepared by other patent processes. We give the composition of some such samples :—

Oil, moisture, etc.	7·40	6·34	7·04
Lead carbonate	50·11	49·96	57·02
Lead hydroxide	42·49	43·70	35·94
	100·00	100·00	100·00

The following is a type of the enormous number of adulterated samples that are frequently met with :—

Oil	11·23
Sulphate of lead	53·84
Sulphates of lime and baryta	28·83
Zinc oxide	6·10
	100·00

A pigment of astounding composition, sold as granitic flat white and ground in oil, contained—

Oil	7·9
White lead	42·7
Zinc sulphide	9·5
Barium sulphate	39·9
	100·0

This on treatment with dilute acid evolved sulphuretted hydrogen with blackening of the pigment. It is a most unsuitable mixture for a white pigment.

Undoubtedly much of the excellence of white lead as a pigment is due to its peculiar composition; lead carbonate is a very fine opaque white of remarkable covering power, but alone it is neither chemically nor physically permanent as an oil colour, as is shown by Prof. Church's experiments quoted in chapter ii. (p. 48), and the experiments quoted by Mr. Laurie, and referred to in our introductory remarks on this pigment; lead hydroxide, though not possessed of great pigmentary value, confers on the substance the most useful property of really combining with the oil in which it is ground, and, on drying, forming a hard and tough varnishy coat of oxidised oil and lead soap.[1] It is for these two reasons that a white lead, containing an excessive amount of carbonate, though beautifully white, is not very durable in oil on the one hand, and one too rich in hydroxide is possessed of but little covering power or opacity on the other.

[1] On grinding with oil some increase of temperature is usually noted; it is generally supposed that this is indicative of some saponifying process being set up, and when one reflects that lead plaster is prepared by warming litharge and olive oil, it is not surprising that a (probably) much more active substance, finely ground lead hydroxide, should act in this way. That some sort of saponification goes on is certain; ether will not extract the oil completely from white lead, but when the apparently oil-free powder is decomposed with acid some traces of oil are usually found.

The preference by painters for old white lead is easily explained when we consider that more saponification may be supposed to have taken place in such samples than in the freshly ground material.

One reason, it would appear, of the superiority of stack corroded over precipitated white lead is that the former is always amorphous, while the latter is usually crystalline; this being the case, however finely the pigment is ground, it is more transparent than the amorphous variety, and probably more light is lost by internal reflection, so that the brilliance, which is always desirable in a white pigment, is somewhat reduced.

The high price of white lead, consequent on the use of a somewhat costly raw material, and the lengthy nature of the process of manufacture, offers great incentive to adulteration and substitution. Various substitutes have been proposed and are sold as better than white lead, and a good deal is done in the way of dilution, or, as it is called, lowering with other white pigments, of which barium sulphate is one of the most used (and cheapest). This fact renders the examination of this material a matter of some importance, and we therefore give a brief scheme for its analysis.

The objects of an analysis of white lead being twofold, (*a*) to determine the presence and, if present, the nature of impurities; and (*b*) to ascertain the proportion of hydroxide and carbonate. The following scheme will be found sufficient:—

Determination of Oil.—A portion of 4 to 7 grams of the pigment ground in oil is weighed into a glass tube of about 30 cc. capacity and 20 cc. of ether added. The tube is corked, and agitated until the white is uniformly diffused in the liquid, and then it is placed in an upright position for some hours until the pigment has settled to the bottom, and then 5 cc. is pipetted off into a weighed beaker without disturbing the deposit, and the oil weighed after all the ether is evaporated. This method is sufficiently accurate for this purpose, though no correction is made for the volume of the oil present in the paint. How small this would be is shown by the following example:—

Suppose 4 grams of a sample containing 8 per cent. of oil were treated with 20 cc. of ether and 5 cc. pipetted off and considered as $\frac{1}{4}$. Eight per cent. of 4 grams is ·32 grams or ·34 cc. of oil. If this dissolved in ether suffers no contraction of volume, the whole volume of liquid will be 20·34 cc., and 5 cc. will be ·246 of the whole instead of ·250, and the weight of oil obtained will be ·079 gram, equal to a result of 7·9 per cent. instead of 8·0 per cent., well within other errors of experiment! The rest of the ether should be poured off this extracted portion of white, and one or two washings added to free from mechanically adhering oil, and the lead and carbonic anhydride determined in this.

Determination of Lead, etc.—(1) About 1 gram of the pigment, either oil-free or ground in oil, is weighed into a beaker and treated with dilute nitric acid, the solution of the lead being hastened by warming either over a small flame or in the water bath. It is necessary that the beaker should be covered, as otherwise loss may occur by effervescence. When all action is judged to be over the liquid is filtered from oil and any other insoluble matter. The filter is washed with hot water and ignited with any insoluble matter (unless there is a great deal, when it should be burnt apart, and the insoluble matter added to the ashes) in a porcelain crucible. Occasionally a trace of lead is retained by the oil, and appears as insoluble matter, in which case its amount should be added to the total lead. If more than 1 per cent. of insoluble matter is found its nature should be determined. Lead sulphate would be sufficiently soluble in strong hydrochloric acid to give a precipitate of barium sulphate with barium chloride and of lead sulphide with sulphuretted hydrogen in very dilute solution. Barium sulphate would be entirely insoluble in HCl, but on fusion with alkaline carbonates (fusion mixture) would yield barium carbonate and alkaline sulphates, and either the Ba or the SO_3 determined as $BaSO_4$ would give the actual weight of

barytes present. The filtrate and washings will contain all the lead (except part of any existing as sulphate) and other metals present. It should be diluted somewhat, nearly neutralised with sodium carbonate, and sodium acetate added, so that any acidity is due only to acetic acid. An excess of neutral potassium chromate is added to the warm solution, which is allowed to stand until the yellow precipitate of lead chromate has subsided, when the supernatant liquid should be poured off through a weighed filter and the precipitate washed once or twice by decantation with hot water, brought on to the filter and washed there, and when free from all salts, as shown by evaporating a few drops of the filtrate on a glass slip, precipitate and filter may be dried in the water oven until of constant weight. The precipitate can, if preferred, be detached from the paper as completely as possible, the latter burnt carefully and the ash moistened with nitric acid and gently incinerated, and then the whole precipitate added to the (porcelain) crucible and gently ignited. The weight of lead chromate obtained $\times$ 0·689 = PbO or $\times$ 0·639 = Pb. The filtrate from the lead should be tested with ammonium oxalate for lime, which if present can be estimated by collecting the precipitate of calcium oxalate and weighing as $CaCO_3$ or CaO. The following mode of procedure (2) is perhaps more satisfactory in the case of adulterated samples. About 1 gram of the sample is treated with diluted hydrochloric acid on the water-bath in a moderate-sized beaker, and the liquid, when all action has ceased, diluted with boiling water and either kept on the water-bath or boiled over a flame. The hot liquid is filtered, the filter paper washed, any insoluble matter examined as above, and the filtrate largely diluted and cooled. To the cooled liquid sulphuretted hydrogen solution is added, or (better) the gas is passed through it until it smells strongly. The precipitate is collected on a filter and washed

with water with a little H_2S dissolved in it, dried, transferred as completely as possible to a crucible and either treated with HCl to convert into $PbCl_2$, or with H_2SO_4 to convert into $PbSO_4$. The former should be dried at 200° C., the latter may be gently ignited until all free SO_3 is evolved. Lead sulphide precipitated in HCl solution is never free from $PbCl_2$, consequently it is best to convert to $PbCl_2$ or $PbSO_4$.

$$PbCl_2 \times 0{\cdot}802 = PbO.$$
$$PbSO_4 \times 0{\cdot}735 = PbO.$$

The filtrate from the PbS should be examined for lime, which if present should be determined.

Precipitation as sulphate of lead in the possible presence of lime is inadmissible ; if, however, SO_3 is found to be present in the sample it is best to treat a weighed portion with HCl or HNO_3, dilute, filter if necessary, and determine the SO_3 either (with the addition of alcohol) as $PbSO_4$ or (much better) by addition of barium chloride and precipitation as $BaSO_4$. The weight of SO_3 found should be added to any found in the insoluble portion as $PbSO_4$, and according as $PbSO_4$, or lime, is present, calculated as lead sulphate or calcium sulphate.

Determination of Carbonic Anhydride.—A portion of 4 to 6 grams of the oil-free pigment is either decomposed in a small flask and the CO_2, after being freed from HCl by copper sulphate (on pumice) and dried by sulphuric acid, is absorbed by caustic potash or soda lime, the increase in weight of potash balls or soda-lime tubes being equal to the amount of CO_2 present, or (less satisfactorily) a loss apparatus of the Schrötter type is used. The percentage of CO_2 is calculated back to the original white in oil,

$$CO_2 \times 6{\cdot}066 = PbCO_3.$$

All the CO_2 found, except in cases where lime is present and SO_3 absent, is calculated as $PbCO_3$, but should lime be

present and no SO_3, all the CO_2 not required to form $CaCO_3$ is calculated as $PbCO_3$, and the excess of lead oxide over the amount required for the CO_2 calculated to $Pb(OH)_2$; $PbO \times 1{\cdot}08 = Pb(OH)_2$. The ratio $PbCO_3$: $Pb(OH)_2$ is thus obtained. Lead sulphate, lime compounds, barytes or china clay can only be regarded as adulterants ; the only object of adding them is to reduce the cost, and their presence and amount should be stated with, we think, a decidedly adverse comment should calcium sulphate be present, as this is more or less liable to be acted on by water. The others are quite inert, and though they decrease the covering power of the pigment, in some cases the lower price of the article may be considered as a set-off against this ; any amount of such diluents is, in our opinion, objectionable, as by their presence the peculiarly good qualities of white lead are reduced.

White lead is usually used in oil, both as a white paint and as priming or preliminary coats to a new surface which is finally to be coloured. The colouring matter or "stain" is seldom applied alone, but is diluted with white, in most cases preferably white lead, to the required tint. By this means colours of poor covering power or bad drying properties will form an opaque, quick drying, tough and impervious coat. It is as an oil colour that the peculiar excellencies of white lead, both as a protective coating to wood or iron and as a covering substance from the colour point of view, are most apparent. White lead will, however, work well in water, and was formerly used considerably when a white pigment was required for water colour. It is not, however, nearly so suitable for this purpose as other white pigments which will be dealt with in this chapter. White lead is known to the artist in oils as flake white and is one of his most important pigments, being used both as a priming for his ground, for diluting other colours and for putting in high lights, either white or white glazed over with other transparent colours. It works well

with most other colours, but is inapplicable in conjunction with coloured sulphides which are liable to cause blackening by formation of lead sulphide. The yellowing by age of flake white in oil paintings has been before alluded to; it seems to be rather a change of the lead-oil varnish than any ordinary deterioration, and is not often so pronounced as to be unpleasant.

Zinc White.

This extremely brilliant white pigment was introduced some years ago in the hope that it might replace white lead. This it has altogether failed to do; it is nevertheless a very fine pigment and possesses very fair covering power, not, however, equal to that of white lead. Its colour is rather a bluish white. It works well in oil and extremely so in water, and is *the* water-colour white *par excellence.*

Zinc white is the only definitely known oxide of zinc; its composition, expressed by the formula ZnO, corresponds to the known salts of zinc. It is prepared by distilling zinc in clay retorts connected with a series of chambers through which air is blown. The zinc volatilises and combines with oxygen in so doing, and the clouds of zinc oxide formed collect on the walls of the receiving chambers as an amorphous deposit easily reducible to powder. This is levigated to separate from any unaltered zinc, and the settled and finely ground oxide collected and dried. It is then ready for mixing with either oil or water. Zinc white can also be prepared by oxidising zinc in large muffles.

As it is a very high-priced material, zinc oxide is subject to considerable adulteration with other less expensive whites. The following scheme will suffice to detect and determine any ordinary adulteration :—

Determination of Oil.—As suggested for white lead (p. 90).

A correction should be made for the volume of oil in solution in the manner suggested.

Determination of Zinc and of Impurities.—A portion of 1 to 2 grams is digested with dilute hydrochloric acid on the water bath or over a flame until all is dissolved (except oil) or until no further solution takes place. The liquid is then filtered and the filter paper with any insoluble matter ignited and the nature of this insoluble portion determined as described under white lead (p. 91). The filtrate is diluted to a known bulk and the zinc determined in a portion corresponding to from ·5 to 1·0 gram of the original, either (1) by titration with potassium ferrocyanide or (2) by precipitation as sulphide.

(1) Titration with ferrocyanide. A solution of potassium ferrocyanide containing 41·25 grams of the salt per litre is standardised by means of pure zinc. About ·5 gram of zinc foil is carefully weighed and dissolved in dilute HCl. The solution is raised to boiling, two or three drops of a solution of uranium nitrate or acetate added and the ferrocyanide solution run in from a burette until the brown colour which at first forms and disappears almost at once becomes more persistent. When this is the case portions are taken out of the vessel on the end of the rod used for stirring and tested with uranium on a tile until a reddish brown colour is produced. This indicates excess of ferrocyanide; the volume used should be noted, ·1 cc. deducted for the amount required to produce the colour and the value of 1 cc. in zinc calculated; this should be ·01 gram almost exactly. The titration of the solution containing zinc should be made in exactly the same way as that with pure zinc. The method is expeditious and accurate, copper and iron being the only interfering substances. Neither is likely to be present in zinc white, but copper gives a chocolate and iron a blue precipitate with ferrocyanide, so their presence would soon be

noted. When the zinc ferrocyanide has settled and left a clear supernatant liquid this can be decanted and tested for lime. The addition of sulphuretted hydrogen to another portion of the original liquid will indicate the presence or absence of lead. Any other white than white lead or calcium carbonate would be found in the insoluble portion.

The zinc found is of course calculated as ZnO. The percentages of zinc oxide, oil and insoluble matter should add up to 100 approximately, if no calcium carbonate or white lead be present. Should either lime or lead be found and it is desired to determine their amount by a direct method—

(2) A definite portion of the HCl solution is treated with sulphuretted hydrogen, being previously considerably diluted if it is not already fairly dilute. Any precipitate in this acid solution is probably lead sulphide. This should be collected on a filter, washed with H_2S water (diluted), dried and weighed as sulphate. This can be examined qualitatively if desired. The filtrate is made alkaline with ammonia, allowed to stand for some time, and the resulting precipitate of zinc sulphide collected on a filter, washed, redissolved in dilute HCl and zinc carbonate precipitated by Na_2CO_3. This is collected, washed, dried and ignited (the filter being ignited separately and the ash added), and weighed as ZnO. Or the dissolved zinc sulphide may be titrated with ferrocyanide as above (1).

We give the results of examination of some samples of this pigment which have come under our notice.

Oil	17·93	17·72	19·17	20·6
Zinc oxide . . .	82·07	82·28	80·83	79·4
	100·00	100·00	100·00	100·00

The above samples as will be seen were all pure. The amount of oil necessary for grinding to a pasty consistency varies a few per cent. either side of 20 (of the whole, or 25

per cent. of the weight of white). The following is the composition of an adulterated sample we have recently met with.

Oil	14·0
Zinc oxide	56·8
Zinc sulphide	21·0
Barium sulphate	8·2
	100·0

Zinc sulphide is sometimes used as zinc white and its use seems quite legitimate, but this sample is also diluted with barium sulphate. It looks like an order made up when the stock of oxide had run short. The reduced proportion of oil is very marked, though the sample was quite as pasty as is usually the case. The sample was of a very bluish white.

The following is typical of many samples we have met with :—

Zinc oxide	56·0
Barium sulphate	34·5
Chalk	9·5

One advantage of zinc oxide is its absolute permanency in sulphur-laden atmospheres. Mr. H. Smith's experiments quoted previously show that as a protective colour zinc white takes a very high rank, and this notwithstanding the general opinion that it is absolutely inert to linseed oil. It would certainly at first sight appear that the oxide of so strongly electro-positive a metal as zinc should have some saponifying action on oil and not be, as is supposed, merely suspended in the hardened oxidised oil coating.

Zinc white in water colour is usually known as Chinese white.

Enamel white (*Blanc Fixe, Permanent White, Barytes White, Barium Sulphate*).

Barium sulphate occurs in nature as barytes, barite, heavy spar, or schwerspath, in crystals of the orthorhombic series.

It should be fairly pure, and require no further preparation than grinding to a fine powder and treating with hydrochloric acid to remove any soluble matters.

Barytes is used to some slight extent as an oil white, but is too crystalline, and, therefore, transparent, to be of much use. Its principal use, or abuse, is to dilute white lead and other expensive colours. Its specific gravity, 4·3 to 4·72, is in its favour for such purposes.

It should be entirely insoluble in hydrochloric acid; any effervescence would indicate the presence of carbonate. The insoluble matter, on fusion with mixed carbonates of potash and soda, should, on extracting with water and treating the aqueous solution with hydrochloric acid until acid, and then precipitating with barium chloride, yield its own weight of barium sulphate, or the insoluble portion dissolved in hydrochloric acid and precipitated with sulphuric acid should also yield its own weight of barium sulphate.

On fusion

$$Ba\,SO_4 + M'_2\,CO_3 = Ba\,CO_3 + M_2\,SO_4;$$

therefore the weights of barium sulphate obtained by either precipitating the Ba or the SO_4 should be equal.

Whitening, Chalk (*Calcium Carbonate*).

Prepared chalk or whitening obtained from native chalk by a process of washing over is used to some extent as a diluent in oil colours, and also for tempera ("distemper") and whitewash. It is, as sold, tolerably pure calcium carbonate, $CaCO_3$. It should be entirely soluble in dilute hydrochloric acid (absence of sand, clay, etc.) to a colourless

solution, give no precipitate when ammonia is added in slight excess to this solution in the presence of ammonium chloride (enough of this is usually formed in neutralising the excess of hydrochloric acid), indicating the absence of iron and alumina. More than traces of iron would spoil the pure white of calcium carbonate. It should, on determination of CaO and CO_2, agree closely with the composition :—

CaO	56
CO_2	44
	100·0

II.—OXIDES OF LEAD.

Red Lead (*Synonym—Minium* Pb_3O_4).

This very brilliant scarlet, or rather perhaps scarlet-pink lead pigment is not now very much used alone, but principally mixed with white lead as a priming coat. It is possessed of remarkable drying properties in oil, and forms a splendid varnishy compound with it. It is usually used with raw linseed oil, as it dries too quickly and with a too brittle surface if used with boiled oil.

Red lead is prepared by heating massicot or litharge (PbO) in furnaces to a temperature not exceeding 300° C. Under these conditions it absorbs oxygen from the air, and is converted into the red powder known as red lead. It is usually supposed to have the composition $Pb_3O_4 = 2PbO\ PbO_2$, but Mulder has found samples of the composition $Pb_4O_5 = 3PbO\ PbO_2$.

We have examined many samples of this pigment, and have found the percentage of lead to correspond tolerably well with Pb_3O_4, though the difference in percentage composition of the two oxides is not great, as the following figures show :—

	Pb_3O_4	Pb_4O_5
Lead	90·66	91·18
Oxygen	9·34	8·82
	100·00	100·00

The following percentages of lead were obtained by us in some of the samples examined :—

89·90, 90·28, 89·60, 91·38, 91·09, 89·94.

Amounts of insoluble matter never greater than 1 per cent. have been found by us ; this insoluble matter appeared to be sand or clay, and was without doubt accidental.

Red lead has a specific gravity of 8·62 – 9·19, is crystalline in structure, darkens on heating, but recovers its colour, and on heating very strongly gives off oxygen. It is not entirely dissolved, but is darkened, by nitric acid, which dissolves out the monoxide as lead nitrate, and leaves the dioxide PbO_2 as a purple-brown powder.

Red lead will dissolve easily in nitric acid if a little sugar or starch is added. This is oxidised partly at the expense of the lead dioxide, and if the acid is somewhat dilute the lead passes into solution as plumbic nitrate ; if the acid is concentrated the nitrate separates in crystals, but can be dissolved by dilution with water. The lead can be determined in this solution, after filtration from any insoluble matter, which should be weighed, by either of the methods recommended in the section on white lead. Red lead also dissolves in hydrochloric acid with evolution of chlorine. If it is decided to determine the lead either as chloride or sulphide, hydrochloric acid is a suitable solvent. The action of hydrochloric acid on red lead affords a means of determining the proportion of dioxide. When lead dioxide or red lead is treated with hydrochloric acid,

$$PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O,$$

or

$$Pb_3O_4 + 8HCl = 3PbCl_2 + Cl_2 + 2H_2O.$$

If the chlorine thus liberated be passed into a solution of potassium iodide, using a suitable form of distilling and absorbing apparatus to ensure complete absorption, then an equivalent amount of iodine is liberated,

$$2K1 + Cl_2 = 2KCl + I_2.$$

This iodine may be titrated with standardized thiosulphate and so, indirectly, the amount of peroxide contained in the red lead determined. For technical purposes it is usually sufficient to ascertain that it is a pure oxide of lead of the right shade.

Litharge (*Massicot, Lead Monoxide, PbO*).

In addition to the hydrated carbonate and the red oxide of lead, the monoxide, litharge or massicot, is used to some extent. This is prepared by heating lead to above its melting point in the open air. It forms a reddish-yellow scaly mass, or an amorphous powder, according to whether the temperature has been sufficiently high to cause fusion. It possesses marked basic properties, and easily enters into combination with oils to form lead soaps. For this reason it is used with linseed oil as a "drying" material. It dries too well to be suitable for use as a pigment, as the coat formed is too hard to wear well. Its principal use is as a drying material for paints and oil varnishes.

Some other lead pigments but little used now are:—

Red-brown, formed by the fusion in a clay crucible of 1 part red oxide of iron with 10 parts of red lead.

Orange mineral, a variety of red lead formed by the calcination of white lead. Mulder gives its composition as:—

Lead monoxide (PbO)	73
Lead dioxide (PbO_2)	25
Carbonic anhydride (CO_2).	2
	100

Mr. A. P. Laurie in his Cantor Lectures says of red lead : "It was prepared by roasting white lead. It is now, I believe, usually prepared from litharge. No doubt the minium prepared from white lead would be a finer pigment."

III.—MERCURY PIGMENTS.

Vermilion.

This very fine scarlet pigment is a sulphide of mercury corresponding in composition with the mineral cinnabar—mercuric sulphide HgS, in fact; occasionally specimens of cinnabar are found sufficiently bright for use as a pigment, more often, however, vermilion is prepared artificially from mercury and sulphur.

There are two classes of processes by which this pigment is prepared—dry processes in which the combination is effected by means of dry heat, and the product prepared by sublimation, and wet processes in which both the combination and further preparation are effected by the aid of liquids.

The procedure in both processes is first to prepare the substance known as Ethiops mineral, a blackish sulphide of mercury with uncombined sulphur, and then by suitable treatment to produce some molecular change by which the substance becomes of a bright scarlet colour.

We give some examples of each class of processes :—

Dry Processes.

At the mines in Idria the following process is adopted—85 parts of mercury and 15 parts of sulphur are ground together in revolving tuns for some hours until combination appears to be complete. The "Ethiops" thus formed is then heated in cast-iron cylinders and sublimed thence into clay condensers.

The process used in Holland is said to consist in preparing the "Ethiops" with 1 part sulphur, 2 parts mercury + 2·5 per cent. finely divided lead or red lead. Lots of about 100 kilos are sublimed and the sublimate allowed to cool slowly during twenty hours, and then finely ground and levigated.

Another process is to gently heat 75 kilos sulphur, and 540 kilos mercury on a shallow iron pan, and break up the "Ethiops," which is kept in jars until it is wished to sublime it. The contents of two or three jars are emptied into a tall clay pot, the bottom of which is heated in a furnace to a dull red. The substance inflames as it is thrown in owing to the combustion of the excess of sulphur, and as the flame goes down a stout well-fitting iron cover is placed on the pot. A fresh charge is added every four to five hours, and the heating continued for thirty-six hours. After cooling the pot is broken, and the vermilion scraped from the lid and top of the pot. The sublimate is then finely ground and levigated.

The shade is sometimes modified by treating with hot alkaline solutions which, perhaps by removing traces of uncombined sulphur, possibly by favouring some molecular change, brighten and purify the colour.

The object of sublimation appears to be twofold, firstly, to remove excess of sulphur, which as being the cheaper material is always used in considerable excess, as the percentage composition of mercuric sulphide shows:—

Mercury	86·2	S : Hg = 1 : 6·2
Sulphur	13·8	
	100·0	

and, secondly, to cause the change which results in the formation of a scarlet sulphide.

Wet Processes.

In China vermilion of a high quality has been prepared probably for many centuries. The process used is supposed to be a wet one.[1]

We give some examples of European wet processes :—

Kirchoff's Process.—Three hundred parts mercury and 68 parts sulphur are moistened with a little potassium hydroxide (caustic potash), and ground together for some time. The black "Ethiops" which forms is then mixed with 160 parts

[1] The following process, which is certainly not a wet one, is given in Thorpe's *Dictionary of Applied Chemistry* as that by which Chinese vermilion "is said to be prepared".

"About half a bottle (38 lb.) of mercury and 17⅓ lb. of sulphur are mixed in an iron pan about twenty-five inches wide and seven or eight inches deep, heated by charcoal. When melted it is stirred with an iron spatula, and the remainder of the bottle of mercury is gradually added. When the metal has disappeared it is removed from the fire, cooled by the addition of a little water, rapidly stirred and coarsely powdered. The reddish or black semicrystalline powder, which contains free mercury and sulphur, is placed in a fixed iron pan, and covered with porcelain tiles eight inches in diameter (many of which are broken), arranged in the shape of a dome. The whole is covered by a pan four inches in diameter less than the fixed one, to which it is luted by clay, leaving four holes in the luting for the escape of gases. The charcoal fire is then lighted and kept fiercely burning for eighteen hours; blue flames are seen burning round the holes, showing loss of sulphur and of mercury. The fires are then allowed to die out, and the pans to cool. Most of the vermilion is found adherent to the porcelain and is removed. That attached to the iron is inferior, and is made with the other waste into cakes with alum and glue-water, dried and resublimed. The sulphide on the porcelain is blood red and crystalline. It is powdered and ground with water in a hand-mill between stones, and washed in a vessel. At the close of a day's work, a solution of alum and glue (1 ounce of each to 1 gallon of solution) is stirred well with the powder, and the whole is allowed to stand until morning. The glue tends to lengthen the period of deposition, and to render the stratification into the various qualities more perfect. The alum is said to improve the colour. The liquid is decanted, and the upper portions of the deposit are set aside. The lower parts are reground and treated as before, the grinding being sometimes repeated several times. The fine vermilion is stirred in water and settled, and the water is decanted. The residue is dried in the open air, powdered, sifted through muslin and packed in papers holding about 1⅓ ounce each."

of potassium hydroxide dissolved in a very little water and heated to boiling for thirty minutes. Water is added to keep up the volume of the pasty mass, which is stirred well, and first becomes brown and gelatinous and then red. This mass is stirred until cold, and then washed free of alkali, ground and levigated.

Brünner's Process.—Three hundred grams mercury, 114 grams sulphur and 75 grams potassium hydroxide dissolved in 450 cc. water are taken. The mercury and sulphur are ground together, and the alkali poured on the mixture in small portions until all is added. The mass is well stirred, and then heated for seven to eight hours at a temperature of 45° to 50° C., the volume being maintained by additions of water. The mixture, which is black to begin with, under the action of the alkali becomes brown, red, and finally scarlet. The vermilion is well washed from all alkali, ground and levigated.

Jacquelin used a similar process, but the following proportions, 90 parts mercury, 30 parts sulphur, 20 parts potassium hydroxide, 30 parts water, and heated to 80° for one hour instead of seven to eight hours at 45° to 50°.

Firmerich prepared a very fine vermilion by the action of (penta)sulphide of potassium on mercury.

Potassium sulphide is prepared by igniting potassium sulphate with charcoal, extracting with water and concentrating to remove unaltered sulphate, which, by reason of its somewhat sparing solubility, crystallises out. The solution of sulphide thus prepared is boiled with sulphur. By this means the polysulphide is formed. This method is found to be more satisfactory than fusion of potassium hydroxide or carbonate with sulphur, as in these methods other products than penta- or other poly-sulphides are formed. Five parts of mercury, 1 part of sulphur, and $2\frac{1}{4}$ parts of sulphide solution (on the basis of 2 parts K_2S to 7 parts

water) are placed in bottles, moderately heated to start action, and continually shaken for three and a half hours; a greenish-brown product results. This is cooled and kept for two to three days in the "stoveroom" at a temperature of 45° to 50° C.; after cooling, the vermilion is carefully treated with sodium hydroxide to remove unaltered sulphur, and the alkali is then removed by washing with water.

The object of the addition of sulphur to the mixture of polysulphide and mercury is to replenish the former substance, which acts as a carrier of sulphur, and to effect a combination which would otherwise require the aid of a dry heat. In the other wet processes the solution of potassium hydroxide used, by causing the formation of sulphides and other sulphur compounds, enables the whole, or nearly the whole, of the mercury used to be converted into sulphide.

Various means are used to improve and to fix the colour of vermilion prepared by either process. Treatment with nitric acid to remove any uncombined sulphur; with a mixture of potassium sulphide and hydroxide with hydrochloric acid, which should remove any alkalies; and with hot potassium hydroxide solution, which is said to give a violet tinge, are processes which have been recommended for these purposes. The main object seems to be to obtain a very pure red material corresponding, as far as is reasonably possible, to pure HgS. This, whatever tint may be obtained, is less likely to alter in tint than a substance which is not a chemical individual.

The examination of vermilion is not usually a matter of great difficulty. It is generally sufficient to agitate a portion with alcohol, and allow to settle, filter off the alcohol, and notice the colour of the solution, and determine the amount of ash left on ignition at a moderately low temperature. The former test indicates the presence or absence of eosin, which would give a pink colour and coppery fluores-

cence to the alcohol, or of other dyes which might be used to brighten the pigment, while the presence or absence of any amount of ash is a criterion of the amount of inorganic adulteration.

Red lead and scarlet antimony sulphide are, we believe, used more or less as adulterants. These, unless present in considerable quantity, have no great effect on the colour of the pigment, though, are of course, undesirable. A mixture of barium sulphate, red lead, a little vermilion, and eosin to brighten the mixture, forms a not uncommon substitute for vermilion. If any residue over 1 or 2 per cent. is left in ignition it is well to examine its nature with a view to detecting adulteration or carelessness in manufacture. Small quantities of ferric oxide (under 1 per cent.) are frequently found in vermilion. This is, doubtless, derived from the vessels used in manufacture, and in such small quantities must be regarded as accidental and allowable, though a treatment with warm dilute hydrochloric acid should remove the greater part of this impurity. Alkali, or alkaline salts, other than mere traces, would indicate imperfect washing and probable formation by a wet process.

Eosin is sometimes added to a pure vermilion, not, in this case, to cover the admixture of a white substance, but to brighten a badly prepared and probably over-heated pigment. In any case its fugitive nature renders its presence in colour intended for any but the most temporary purposes extremely undesirable.

Chinese vermilion, which is greatly esteemed for its beautiful full colour, usually contains a small quantity of organic matter, apparently glue, but not in sufficient quantity to be in any way objectionable.

Should it be considered in any way desirable to determine the mercury in this substance, a portion of, say, 10 grams should be mixed with pure quicklime and " burnt " in a com-

bustion tube packed in the usual manner. The arrangement of the ingredients in the tube, starting from the front end, is as follows :—

Lime and iron or copper.
Vermilion and lime.
CO_2 mixture.

The best plan is to weigh the vermilion on to 10 to 20 grams of freshly ignited lime in a glass or porcelain mortar, and then fill in, either by a funnel or by scooping with the tube itself into a clean dry combustion tube of about $\frac{3}{8}$ to $\frac{1}{2}$ inch internal diameter, closed at one end, and with 2 to 3 inches of a substance to evolve CO_2,[1] already filled into the closed end, and plugged down with asbestos.

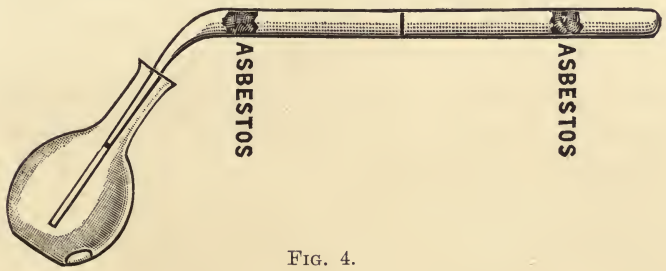


FIG. 4.

The mortar is then rinsed out with one washing of lime, and a plug of asbestos inserted in the tube, after which a further portion of lime is filled in. A layer of copper turnings, gauze

[1] The following substances are suitable to use for the evolution of CO_2 :—

1. A mixture of 3 parts fused potassium bichromate with 1 part of ignited anhydrous sodium carbonate, both finely powdered, and then intimately mixed. This is a very good and sensitive mixture. On ignition—

$$K_2Cr_2O_7 + Na_2CO_3 = K_2CrO_4 + Na_2CrO_4 + CO_2.$$

2. Sodium bicarbonate. On ignition—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

3. Magnesite. On ignition—

$$MgCO_3 = MgO + CO_2.$$

4. Oxalic acid, anhydrous. On ignition—

$$\begin{matrix} COOH \\ COOH \end{matrix} = CO_2 + CO + OH_2.$$

1 and 3, which give *dry* CO_2, are preferable.

or spirals of wire, or of iron nails or wire, about 3 inches long, is then filled in, and the tube drawn out obliquely and (when cooled) placed in a combustion furnace, the drawn-out part dipping well below the surface of water in a flask or beaker. The heating is started from the open end of the tube, and when 3 to 4 inches of lime are red hot, one burner at a time should be lit, and also one burner at the back under the plug of asbestos by the CO_2 mixture to prevent sublimation back, and to start a stream of CO_2, which should be maintained, so as to secure constant bubbling of gas through the water (thereby preventing a back rush of water). When the whole of the lime is red hot all the burners should be lit so as to sweep over all the mercury vapour. Then, when no more globules of mercury condense, the curved part of the tube is broken by touching it with a wet file or glass rod, and any mercury which may have accumulated in this front part is washed into the flask and gently agitated to cause the globules to cohere, the water poured off as completely as may be, and the mercury transferred to a weighed porcelain capsule, the visible water being removed by blotting paper, and the mercury dried at a low temperature in a desiccator and weighed.

The use of copper or iron is necessary in the case of mercuric sulphide, as otherwise sulphide may sublime over, or, if water vapour be present, sulphuretted hydrogen be formed. In either case the heated metal retains the sulphur and allows the mercury to pass over.

The action of the lime may be represented as follows :—

$$2HgS + 2CaO = 2CaS + 2Hg + O_2.$$

Some of the calcium sulphide is probably oxidised to sulphate by the oxygen liberated.

The action of the iron or copper is :—

$$M'' + HgS = M''S + Hg,$$

or

$$M'' + H_2S = M''S + H_2.$$

This dry distillation method is very accurate indeed, but in ordinary work is certainly seldom necessary.

When vermilion ground in oil is examined a portion should be freed from oil, as recommended in the case of white lead and other pigments, and eosin looked for in the ethereal solution. The oil-free matter is ignited, and, if necessary, the residue examined. When a determination of the oil is not considered necessary, it will be sufficient to shake up with ether and filter off the solution, examining its colour, and to ignite a portion of the oily material.

The nature of probable adulterants of vermilion has been indicated in the preceding paragraphs. Having regard to the high specific gravity of vermilion, it is obvious that very few adulterants could be used in any amount without so seriously reducing the specific gravity of the material that it would be apparent to the user.

We have occasionally examined adulterated samples of vermilion, and also samples of mercuric sulphide brightened with eosin; doubtless these latter were badly prepared, and "faked" in this manner to avoid the cost of resublimation. The composition of two of these is given below:—

Mercuric sulphide	58·9	50
Barium sulphate	12·0	—
Lead sulphate	29·1	49
Eosin	—	1
	100·0	100

We also give the composition of some genuine samples:—

Moisture	0·4	0·5	—	—
Loss on ignition (HgS)	99·1	99·2	99·1	99·4
Non-volatile matter	0·5	0·3	0·9	0·6
	100·0	100·0	100·0	100·0

The non-volatile matter was either clay or oxide of iron, with traces of alkali in the case of the last sample (= under 0·03 per cent. KHO).

Vermilion, notwithstanding its extreme brilliance and good body, has a rather bad reputation for permanence. It would appear to be somewhat liable to molecular change, as it is stated that exposure to daylight has changed from red to black vermilion letters in illuminated books exhibited in museums, which had remained intact for hundreds of years with the limited exposure incurred in use. It must at the same time be admitted that vermilion frequently will retain its colour for a long time and under trying circumstances. Being a very inert substance and a sulphide, it is not easily changed in composition, or in any way chemically affected by any reasonably possible use except, of course, at very high temperatures, and, as we have before stated, the liability to molecular change appears to be much reduced by careful removal of impurities, and in the case of the dry-formed material by condensation at a high temperature.

It must be remembered that vermilion is used for painting out-door work by both Post Office and Fire Brigade authorities, and that it stands well on their carts and pillar-boxes under very trying conditions. We know that in the case of the Metropolitan Fire Brigade great care is exercised in the selection of vermilion for this work, and doubtless the Postal authorities exercise similar care.

We think that in many modern cases of serious deterioration of so-called vermilion, an examination of the colour would have shown it to be a "vermilionette," the fancy name for adulterated, brightened scarlets, some of which are almost innocent of mercury.

Royal Scarlet (*Mercuric Iodide*).

This pigment is prepared by the double decomposition of solutions of mercuric chloride and potassium iodide. It is, as both these substances are expensive, desirable to use molecular proportions. The proportions 4 mercuric chloride

to 5 potassium iodide agree very closely with those required by the scheme.

$$\underset{271}{HgCl_2} + \underset{332}{2KI} = \underset{454}{HgI_2} + 2KCl.$$

Though a very brilliant colour, mercuric iodide is not to be recommended.

IV.—THE CHROMIUM COLOURS.

Two series of colours owe their tints to the presence of the element chromium, the chromium oxide greens and the yellow and red chromates. The former contain as the colouring group the oxide Cr_2O_3, sometimes as hydroxide, sometimes as phosphate, while the latter owe their colour to chromic anhydride CrO_3.

The Chromium Oxide Greens.

Chromium oxide, Cr_2O_3, prepared by ignition of the hydroxide, or by the methods given below, is a sage green coloured substance easily worked in water or oil, and absolutely permanent as to tint, being not only unaffected by light, but also unattacked by acids or alkalies. It is insoluble in concentrated acids, and can only be brought into solution by fusing with an oxidising mixture such as sodium carbonate and potassium nitrate, or chlorate, when it is converted into chromic anhydride, thus :—

$$Cr_2O_3 + 3O = 2CrO_3.$$

This is found in the product of fusion as alkaline chromate.

On account of its permanency chromium oxide is a colour much esteemed by artists. We give some methods of preparing it ; they are mostly based on the reduction of chromates and bichromates.

(*a*) By the ignition of mercurous chromate (the brick-red precipitate obtained on adding a soluble chromate to a solution of a mercurous salt) a very pure and fine-coloured

oxide is obtained. The process should be carried out in a covered porcelain or earthenware crucible at a dull red heat.

$$4Hg_2CrO_4 = 2Cr_2O_3 + 8Hg + 5O_2.$$

(*b*) Potassium bichromate is ignited with sulphur. Potassium sulphate and chromium oxide are left in the crucible and can be separated by washing. The following scheme may represent the action :—

$$K_2Cr_2O_7 + S = K_2SO_4 + Cr_2O_3.$$

(*c*) Potassium chromate and charcoal are ignited together in a crucible. Potassium oxide and carbonate, and chromic oxide remain.

The melt is treated with boiling water, and after disintegration, the liquid is boiled to precipitate any hydroxide of chromium which may have formed and dissolved in the free alkali, and the insoluble part, after washing, is dried and ignited. Chromium oxide prepared in this way is seldom free from alkali.

(*d*) By the ignition of potassium bichromate with an equal weight of ammonium chloride and a little sodium carbonate a mixture of alkaline chloride and chromic oxide is obtained.

(*e*) On the ignition of ammonium bichromate a violent action with incandescence takes place, and a voluminous green-tea-like residue of chromium oxide remains.

By all the methods described above the green oxide of chromium Cr_2O_3 is obtained. Two other substances closely allied to it are, however, used as green colouring matters—a hydroxide and a phosphate of chromium.

Guignet's green, vividian (veridian), Mittler's green, chromium hydroxide, $Cr_2O_3\ 2H_2O$.

This brilliant emerald green pigment is prepared by the ignition of three parts of boric acid with one part of potassium

bichromate to dull redness for a suitable period. On the small scale we have found one hour sufficient. A copious evolution of oxygen and violent frothing take place; it is therefore advisable to use a large crucible for the fusion. The melt is washed out with hot water, and if the operation has been carried out properly, only a very slight yellow colour should be imparted to the wash water, the whole of the chromate being reduced. It appears that a mixture of potassium and chromium borates is formed, and the latter is, on heating with water, decomposed and hydrolised into chromium hydroxide and boric acid.

The product obtained by us in this manner was a full brilliant green, and after careful washing and drying, first in the air and then in a water oven, it lost on ignition 14·1 per cent. $Cr_2O_3\ 2H_2O$ requires 19·0, $Cr_2O_3\ H_2O$ 10·5. This substance would appear to be a mixture.

We found that by using less boric acid a dull green, which only lost a trace on ignition, and was evidently Cr_2O_3, was obtained, and the action was by no means complete, a good deal of unaltered bichromate being present. This seems to point to the need of sufficient boric acid to form chromium borate in order that the hydroxide and not the oxide may be formed.

A sample of Guignet's green, prepared by M. Kestner, and analysed by a Mr. Shipton, one of Hoffman's pupils, contained boric acid, and on drying at 100° had the following composition:—

Oxide of chromium . . .	76·47
Boric acid[1]	12·10
Water	11·43
	100·00

A sample of "green oxide of chromium," sold by a firm of artists' colourmen of repute, was examined by us. It contained—

[1] By difference.

Oil	27·4
Chromium oxide . . .	66·0
Alumina	5·6
Lime salts, etc. . . .	1·0
	100·0

The proportion of alumina seems larger than might reasonably be present as impurity; it was possibly added to reduce the colour to a standard tint.

A sample of veridian examined by us, from the same maker as the green chromium oxide just noticed above, contained :—

	Oil (loss on ignition less H_2O calculated) .	48·9
	Chromium hydroxide	46·4
After ignition	Matter soluble in water (alkaline chromate)	3·5
	Matter soluble in acid	1·2
		100·0

An actual determination of oil gave 50·3 per cent. This rather tends to show that our calculation of chromium hydroxide as Cr_2O_3 $2H_2O$ from the percentage of Cr_2O_3 was not justified; we suggest this in view of the composition of our own preparation. The unaltered chromate which, perhaps, would brighten the green seems to point to insufficient ignition and subsequent insufficient washings. Its presence is, in our opinion, undesirable.

IVa.—THE CHROMATE COLOURS.

We believe we are correct in stating that all chromates are coloured bodies, but only certain of these compounds, from the beauty of their tint and other considerations, are used as pigments. Of these the principal are the chromates of lead, while less important members of the group are zinc, barium, and strontium chromates.

The Chromates of Lead.

Lead forms two definite compounds with chromic acid—the neutral chromate containing one equivalent of chromic

anhydride and one of lead oxide (PbO), a yellow compound varying in depth of colour according to the conditions of its formation, and represented by the formula $PbCrO_4$, and a basic chromate containing two equivalents of PbO to one of CrO_3, Pb_2CrO_5 (= $PbCrO_4$, PbO), a beautiful red compound. An intermediate substance, probably a mixture, is known as orange chrome.

Normal Lead Chromate Colours *(Chrome Yellow, Paris Yellow, Cologne Yellow, etc.).*

When a neutral or only slightly acid solution of a lead salt is treated with a solution of a chromate a heavy yellow pulverulent precipitate separates, and an alkaline salt is left in solution. In the case of lead acetate and sodium chromate the changes occurring may be represented by the equation—

$$Pb(C_2H_3O_2)_2 + Na_2CrO_4 = PbCrO_4 + 2NaC_2H_3O_2.$$

The compound thus produced is constant whatever the conditions of precipitation; a full yellow, such as pure chromate, is not often used in commerce. Such pure colours are not, however, entirely unknown, one examined by us, ground in oil, had the composition—

Oil	25·0
Lead chromate ($PbCrO_4$)	75·0
	100·0

It is more common to prepare a diluted pigment containing a greater or less percentage of some inert white substance; by this means a range of colours from a full orange yellow to the palest lemon can be obtained.

There are three types of these diluted yellows, (*a*) chromate white lead yellows, (*b*) chromate lead sulphate yellows, (*c*) chromates diluted with whites not containing lead.

(*a*) The first type of yellow, which seems, though not very much used, to be theoretically the most satisfactory, having regard to the excellent drying and covering powers of

white lead, is prepared by treating dry white lead with a quantity of dilute acetic or nitric acid insufficient to entirely dissolve it, and precipitating with alkaline chromate, or more usually bichromate, in insufficient quantity to attack all the dissolved lead. By this means a mixture of lead chromate and white lead is obtained, which varies in colour according to the amount of white lead dissolved. This is allowed to deposit, and washed free from soluble salts.

Two samples, evidently prepared by this method, and called "pure chrome yellow," were almost pure lead chromate of a full colour.

Lead chromate	92·2	93·4
White lead	7·8	6·6
	100·0	100·0

Samples of lemon and orange yellow of this kind had the following composition :—

	Lemon.	Orange.
Lead chromate	31·5	47·7
White lead	59·0	47·2
Insoluble in acid	2·7	—
Difference	6·8	5·1
	100·0	100·0

(*b*) The second type of colours, with lead sulphate as a white base, is always considered by the trade as pure, consisting only of lead compounds. Colours of this kind are usually prepared by precipitating lead acetate or nitrate with mixtures of alkaline bichromate and Glauber's salts (sodium sulphate) or alkaline bichromate and sulphuric acid. Lead chromate and lead sulphate are by this process simultaneously precipitated, and the proportions may be so adjusted as to produce the requisite variety of shades.

Biot and Delisse precipitate lead sulphate by treating lead acetate with sulphuric acid or sodium sulphate, and then digest three parts of the washed precipitate with one part of

potassium chromate in hot water. The conversion of the chromate according to the following scheme—

$$K_2CrO_4 + PbSO_4 = PbCrO_4 + K_2SO_4,$$

is almost complete, and the lead chromate is obtained mixed or combined with the unaltered lead sulphate. By this means a good yellow is produced of very high colour for the amount of chromate used; the covering power is, however, less than that of the precipitated yellow. Lead chloride is converted into chromate in a similar manner.

We have examined some of these colours:—

Lead chromate . . .	57·3	Lead chromate . . .	50·4
Lead sulphate . . .	26·3	Lead sulphate . . .	41·2
Calcium carbonate, etc. .	7·1	White lead	8·4
Insoluble in acid ($BaSO_4$) .	9·3		
	100·0		100·0

Oil	22·2
Lead Chromate . . .	38·8
Lead sulphate . . .	23·2
Sulphate of lime . . .	15·8
	100·0

(*c*) The third class, comprising the cheaper chrome yellows of the kind usually known as Cologne yellow, includes all those colours where the required paleness of tint is obtained by the addition of white substances other than lead compounds, such as sulphate of barium.

Basic Lead Chromates.

The basic compounds (or rather, perhaps, mixtures of lead chromate) include orange chrome and chrome red, the latter being the more basic substance.

These substances are usually prepared by the action of sodium hydroxide on yellow lead chromate, the alkali abstracting the chromic anhydride from a portion of the lead compound, forming alkaline chromate, while basic chromate of lead remains.

$$2PbCrO_4 + 2NaOH = Pb_2CrO_5 + Na_2CrO_4 + H_2O.$$

Basic lead chromate is known as Derby red or Chinese red. It is, when carefully prepared, a very beautiful colour, somewhat resembling vermilion. It is, sometimes at least, a crystalline substance consisting of single rectangular prisms, and it is stated that the brightest shades owe their beauty to the (relatively) large size of the crystals. It is desirable to make small, roughly quantitative experiments to ascertain the proportion of alkali and chromate required to prepare a pigment of the desired colour and to use the same proportions and dilution in the actual preparation.

Liebig and Wöhler prepared vermilion-coloured reds by dropping into a fusion of equal weights of potassium and sodium nitrates, small pieces of chrome yellow. Ebullition occurs and the mass becomes black; it is heated until ebullition ceases. If it is overheated the product becomes brown (? owing to formation of lead dioxide). The melt should be washed quickly.

Another process is to treat a solution of lead acetate with a mixture of potassium hydroxide and chromate.

$$2PbO_2(C_2H_3O)_2 + 2KOH + K_2CrO_4 = Pb_2CrO_5 + 4KO{\cdot}C_2H_3O + OH_2.$$

Prinvolt prepared a chrome red he called Persian red by digesting 25 parts of lead carbonate with 10 parts of potassium chromate dissolved in water, for two days. Basic lead chromate and potassium bichromate (and carbonate) are said to be formed. The liquid is boiled for half an hour, some of the precipitate becomes decomposed and lead chromate is formed, the precipitate turning violet. This is washed and digested with sulphuric acid (1 in 100 water) and the red pigment is the result.

We have examined several samples of Derby red, Chinese red and orange chrome, of which we give the composition.

	Chinese Red.			Derby Red.		
Water and volatile matter	—	—	—	0·7	—	—
Lead oxide (PbO) . .	80·0	80·1	79·8	79·2	79·3	80·8
Chromic anhydride .	16·8	17·2	17·8	18·1	17·5	17·6
Other matters . . .	3·2	2·7	*2·4	2·0	3·2	*1·6
	100·0	100·0	100·0	100·0	100·0	100·0

	Orange Chrome.			
Lead oxide	79·4	80·4	74·5	72·7
Chromic anhydride . .	14·3	12·9	13·9	14·7
Other matters . . .	6·3	6·7	11·6	12·6
CO_2	100·0	100·0	100·0	100·0

In most of the above samples the "other matters" consisted of carbonate of lime, which in small quantity is easily accounted for by the action of alkali on hard water used in manufacture thus:—

$$CaCO_3, H_2CO_3 + 2KOH = CaCO_3 + K_2CO_3 + H_2O$$

The samples marked * were also brightened with eosin (about 0·3 per cent.), which is an undesirable practice.

One sample of Derby red examined by us was not a chrome colour at all. It had the following composition:—

Water	8·5
Loss on ignition	4·0
Ferric oxide	15·9
Alumina	1·1
Sulphate of lime	42·3
Carbonate of lime	3·9
Insoluble siliceous matter	24·3
	100·0

—a similar pigment to the colour known as light red, which is very much cheaper than a lead chromate.

Zinc Chromate ($ZnCrO_4$).

This pigment is prepared by precipitating a solution of zinc sulphate with a solution of sodium or potassium chromate. It is necessary that the zinc salt should be fairly pure

and should be treated with sodium hydroxide or carbonate, which precipitates a small amount of zinc hydroxide or carbonate. The precipitate which is formed on the addition of alkaline chromate is of a pale yellow colour, and only requires washing, drying and grinding to render it suitable for use.

R. Wagner gives the result of the examination of samples of English and German manufacture :—

ENGLISH.

		$ZnCrO_4$.
Chromic anhydride	14·94	55·2
Zinc oxide	75·35	44·8
Carbon dioxide	3·61	—
Water	6·19	—
	100·09	100·0

GERMAN.

Chromic anhydride	11·88	9·21
Zinc oxide	45·78	61·47
Barium sulphate	42·34	29·32
	100·00	100·00

It will be seen that the use of barium sulphate for "lowering" purposes is not an exclusively English custom. All these colours have evidently been prepared by previous precipitation of oxide or carbonate as there is but a very small proportion of CrO_3 present in any of the three.

Zinc chromate is, we believe, only used to a very small extent in commerce. We have never yet examined a sample of this pigment.

Silver Chromate (Ag_2CrO_4).

This blood-red pigment, prepared by the precipitation of neutral solutions of silver nitrate with alkaline chromates, is said to be used to some extent in miniature painting. It is unnecessary to state that it is a very expensive substance, and,

whatever its merits, only suitable for use on the very small scale.

Mercury Chromates.

Mercurous chromate, Hg'_2CrO_4, prepared in a similar manner to silver chromate, has been used as a pigment. It is both costly and easily decomposed by light. It is of a brick-red colour.

Mercuric chromate, $Hg''CrO_4$, prepared by the precipitation of a mercuric solution with alkaline chromate, is a light-red pigment.

We believe neither of these substances has ever been used to any extent as a pigment, nor are they suitable. For the analyses of the chromates of lead and mixed colours containing these compounds the following scheme will be found satisfactory: A suitable quantity (about 1 gram) of the oil-free colour is weighed into a beaker, covered with hydrochloric acid, and the beaker, covered with a watch-glass, placed in the waterbath to digest for fifteen to thirty minutes. At the end of this time the chromate will have been reduced to chromium salt in accordance with the scheme—

$$CrO_3 + 6HCl = CrCl_3 + 3H_2O + 3Cl.$$

The liquid is now diluted with boiling water. The cover and the sides of the beaker are washed to prevent loss of spray and the beaker heated on a flame, with stirring. If any insoluble matter remains it should be well washed with hot water and its nature examined. It is most likely to be either barium or lead sulphate, though the latter would be partly dissolved by hydrochloric acid. The mixed filtrate and washings are treated with sulphuretted hydrogen (after dilution and cooling) and the sulphide of lead collected and treated as described on page 93 (white lead). The excess of H_2S is removed from the filtrate by boiling, a few drops of nitric acid added to oxidise any iron, if present, and ammonium hydroxide

solution added. This precipitates chromium hydroxide, which is collected, washed, ignited (still in the filter paper) in a platinum crucible and weighed as Cr_2O_3. If a preliminary test has indicated the presence of iron this would also be included in this precipitate as Fe_2O_3 and should be estimated by titration, after reduction with $SnCl_2$, with bichromate. Barium or lime would be found in the filtrate from the "ammonia precipitate," which, in this as in all other cases, should after the first precipitation be washed by decantation partly on to the filter, given one or two washings, and then the contents of the filter washed into the beaker used for precipitating, redissolved in HCl, and reprecipitated by ammonia which should be only added in slight excess, the excess being boiled off. Unless this procedure is adopted lime is always likely to be precipitated with the bases of the chromium group. Lime can be determined in the mixed filtrates by precipitation with ammonium oxalate and conversion to carbonate or oxide; barium would also be precipitated by ammonium oxalate, hence it would be well to dissolve the carbonate or oxide when weighed in a large excess in fairly strong HCl, and add sulphuric acid to the hot solution. Under these conditions barium sulphate would be precipitated and calcium sulphate remain in solution. It is, of course, impossible that barium should be present in solution if a preliminary test on the original pigment indicated the presence of sulphates soluble in hydrochloric acid. If these be present the SO_3 should be determined in a fresh portion of the pigment treated with HCl, as already described, by precipitation with barium chloride. Lead sulphate, though almost insoluble in water, is moderately soluble in a large volume of hot HCl.

Having determined the amounts of lead, chromic acid (Cr_2O_3 corresponds to $2CrO_3$), lime, barium and sulphuric anhydride, if present, it now remains to combine these as they really existed in the pigment. If the lead oxide is in excess of

that required for $PbCrO_4$, and the colour of the pigment does not indicate the presence of basic chromate, and SO_3 is absent, it is best to consider the excess as white lead. Lime would be present as sulphate or carbonate, barium as chromate or, if in the insoluble matter, as sulphate. If sulphuric acid is present, and more lead present than required for all the CrO_3, then the SO_3 should be calculated to $PbSO_4$, and if this agrees fairly well with the excess of lead, returned as such, but of course some judgment is required to decide such points. In the case of obviously basic chromates it is best to return PbO and CrO_3 together with such impurities as may be present.

In all cases it is a good plan to determine whether boiling water extracts more than traces of alkaline and other soluble salts, for the presence of these in any quantity is due to careless washing. A sufficiently accurate method for the examination of lead chromate colours is to treat a weighed quantity with HCl, evaporate to dryness and wash with alcohol. Chromium chloride and any chloride of calcium or other probable metals are dissolved, leaving lead chloride, which is insoluble in alcohol and can be weighed. The chromium can be determined in the filtrate, after evaporating off the alcohol, by precipitation with ammonia, and is weighed as Cr_2O_3. Calcium can be determined in the filtrate from the ammonia precipitate. If SO_3 is present, a mixture of $PbSO_4$ and $PbCl_2$ will be left insoluble in alcohol, and a determination of the SO_3 in a separate portion of the pigment should give figures for calculating the actual amount of lead in the mixed sulphate and chloride.

This method we have found more especially useful in the case of chrome red and orange, which are usually fairly pure. Its advantage is that the use of H_2S is not necessary, an advantage in a laboratory which is not isolated from the rest of the world.

The percentage of CrO_3 in chromates may be determined

by passing the chlorine evolved on treatment with HCl, into potassium iodide solution, and titration of the liberated iodine with sodium thiosulphate—

$$R''CrO_4 + 8HCl = R''Cl_2 + CrCl_3 + 3Cl + 4H_2O$$
$$KI + Cl = KCl + I.$$

Brunswick Green.

This pigment is now a mixed colour, prepared by admixture of Prussian blue with lead chromate, a suitable white diluent (usually barytes) being added in sufficient proportion to produce a manageable pigment. It is a rather dullish pure green, and under ordinary conditions is fairly permanent, though chrome yellow has some action, in course of time, on Prussian blue. Brunswick green is very largely used for outdoor work, as painting ornamental ironwork, bridges, railings, gates, etc.

There are two general methods of preparing this green, (*a*) by mixing the constituents ready formed, (*b*) by precipitating the blue and yellow on the finely ground barytes.

The composition of samples of light, middle and dark Brunswick green examined by us is given in the following table :—

	Light.	Middle.	Dark.
Chrome yellow ($PbCrO_4$)	5·59	1·16	10·11
Prussian blue	0·95	0·66	4·96
Barium sulphate	91·74	90·39	79·40
Lime, salts, etc.	1·72	7·79	5·53
	100·00	100·00	100·00

The following paragraphs from the paper on Prussian blue published by us (*Analyst*, 225, 1896) sufficiently describe the method of analysis found by us to be satisfactory :—

"Two samples of Brunswick green ground in oil were examined. Brunswick green is a Prussian blue-lead chromate green mixed with barium sulphate ('barytes'). A portion from which the oil had been extracted was gently ignited

and treated with hydrochloric acid, the solution of lead, iron and chromium chlorides filtered from the barium sulphate, and the lead precipitated with sulphuric acid. In the filtrate from the lead sulphate the 'ammonia precipitate' containing the mixed oxides of iron and chromium was determined. The oxides were separated by fusion with alkaline carbonate and nitrate and extraction of the fused mass with water, Fe_2O_3 being insoluble. Direct titration with $K_2Cr_2O_7$ was difficult, as the colour of the chromium masked the reduction of the iron with stannous chloride :—

	Light Green.	Dark Green.
Oil	11·27	13·55
Prussian blue (Fe × 3·03) . . .	1·01	4·21
Chrome yellow	4·98	7·10
Barium sulphate	82·74	75·14
	100·00	100·00

"The nitrogen was determined in each of these samples in about 5 grams, and was ·19 and ·72 respectively, which, using 4·4 as a multiplier, would give ·83 and 3·16 per cent. of Prussian blue in these samples. We are much more inclined to rely on a direct determination of this kind than on the determination of the iron by the method described. The method of analysis for these colours described by Hurst, and due to Brown (*Chem. News*, 31st December, 1886), seems still more unsatisfactory. The green is treated with hydrochloric acid to dissolve out the lead chromate (of course, as lead and chromium chlorides). The residue, barytes and Prussian blue, is ignited to decompose the blue, weighed, treated with *aqua regia* to dissolve out oxide of iron (*and alkalies*), and the insoluble portion again weighed. The difference is to be taken as oxide of iron, and multiplied by 2·212 to give Prussian blue. The lead and chromium are of course determined in the original filtrate."

V.—IRON OXIDE PIGMENTS.

A most important class of colours, on account both of their very general use, extending to remote antiquity, and of their high intrinsic value, is that array of pigments the colours of which are due to oxide and hydroxide of iron. This class comprises both natural and artificial colours of varied shades of yellow, red, brown and purple; of the natural earths some are darkened in colour by roasting, resulting in the loss of water of hydration and consequent formation of a redder oxide; most or all, however, of the natural earths are also used in their unburnt state.

The composition of these colours is very variable; some of the red and purple pigments are nearly pure ferric oxide (Fe_2O_3), others contain large amounts of silica and lime salts, whilst not infrequently barium sulphate is found as a natural admixture; many of the browns owe their rich colour to the presence of small quantities of oxide of manganese; of the yellows, most are hydrated oxides and silicates of iron, usually considerably diluted by (natural) admixture with lime salts.

In considering this group of pigments we propose to give brief descriptions, first, of the natural earths, raw and "burnt," and then of those members of the group which are usually prepared by more artificial means. It will be convenient to consider the general properties and method of analysis of these colours as a group rather than as individuals.

The Ochres.

There are two distinct series of colours known under the name of ochres, namely, those which owe their colour to hydrated oxide of iron—the yellow and brown ochres, and those which are coloured by the anhydrous oxide—red ochres. Members of the former class, by the simple process of roast-

ing (and consequent dehydration), are converted into the latter.

The ochres essentially consist of ferric hydroxide or oxide, which is usually more or less mixed with clay, sand, lime salts, and occasionally magnesia. The most used ochres are those known collectively as yellow ochres. Yellow ochre is the ὤχρα known to the Greeks in the time of Apelles, used also by the Egyptians and Romans, and also by savage nations in later times for painting their bodies. Its colour is due to yellow hæmatite, *xanthosiderite*, Fe_2O_3, H_2O, brown hæmatite, *limonite*, $2Fe_2O_3$, H_2O, and bog-iron ore, *lymnite*, Fe_2O_3 $3H_2O$; the brown hæmatite, according to Church, being the most commonly occurring.

In England ochres are found in Cornwall, often associated with tin and copper ore and separated from these by elutriation, in Derbyshire and at Shotover Hill in Oxfordshire, not to mention other localities. The beds are usually above the oolite deposit, covered by sandstone and quartzose sands more or less ferruginous, with plastic clays also containing iron. The following sectional measurements of the Shotover deposit are taken from Dr. Ure's dictionary:—

Ferruginous grit (forming summit of hill)	6 feet
Grey sand	3 ,,
Ferruginous concretions	1 ,,
Yellow sand	6 ,,
Cream-coloured loam	4 ,,
Ochre	6 inches

A further deposit of ochre occurs beneath a layer of clay.

A sample of this Oxfordshire ochre examined by Prof. Church contained:—

Hygroscopic moisture	7·1
Combined water	9·0
Ferric oxide	13·2
Alumina	6·3
Silica	61·5
Calcium sulphate	1·4
Undetermined	1·5
	100·0

A sample called Oxford ochre examined by us gave the following figures :—

Oil and water of combination	31·32
Oxide of iron	9·04
Alumina	5·13
Lime salts	5·20
Insoluble matter [1]	49·31
	100·00

[1] Including barytes ($BaSO_4$) 20·62 per cent.

This differs from Church's sample in containing barytes. Though native ochres are very largely used in England, India, France, Italy, Spain and Germany also supply us with considerable amounts of this valuable pigment. The composition of some of these is given below.

Yellow ochre varies considerably in colour, the variation being caused by the presence of different hydroxides of iron and varying amounts of white matter (clay, etc.). It is seldom that the clay contained in ochre is very ferruginous, samples usually leave a fairly white residue on treatment with strong hydrochloric acid. The colour varies from a pale dull yellow to that now known in England, as it had for years been in India, as khaki.

Yellow ochre, being a cheap pigment, is not much subject to adulteration ; barium sulphate is sometimes present, but it is difficult to decide whether this is not naturally occurring, and, in any case, if the tint is suitable, its presence is entirely harmless. Church states that occasionally ochres are brightened by the addition of such organic colours as turmeric. In this case a yellow colour would be imparted to alcohol, or, if the pigment were ground in oil, probably a mixture of alcohol and ether would extract both colour and oil, and the addition of alkali would, by causing change of colour, indicate the presence of turmeric.

Brown ochre is very similar to raw sienna, which is also dealt with in this chapter.

An analysis of brown ochre sold by a firm of artists' colourmen of repute gave the following figures :—

Oil, Water of hydration, etc.	39·0
Ferric oxide	34·6
Alumina	4·7
Lime salts, etc.	6·6
Insoluble siliceous matter	15·1
	100·0

The following analysis of a New Zealand ochre, used as a paint by the natives, given in Dundas Thomson's *Cyclopædia of Chemistry*, is of interest :—

Ferric oxide	64·36
Silica	13·92
Water	20·2
Organic matter	4·72
	103·20

This contained traces of alumina and lime, and gelatinised with acids. The colour of this ochre is not stated.

COMPOSITION OF YELLOW OCHRES.

	French Ochre.	French Ochre.	Stone Ochre.*	"Yellow Ochre."	Stone Ochre.*	Stone Ochre.*	Stone Ochre.*
Water	0·39	9·87	—	1·70	—	—	—
Loss on ignition	7·98		27·8	4·15	38·31	23·37	23·72
Oxide of iron	18·71	33·50	11·2	13·95	43·64	24·75	22·31
Alumina	2·78		4·6				
Lime salts, etc.	·64	—	1·2	3·20	8·05	3·28	0·88
Insoluble in HCl	69·50	56·63	55·2	77·00	10·00	48·60	53·09
	100·00	100·00	100·0	100·00	100·00	100·00	100·00
Barium sulphate	—	—	—	—	—	38·62	51·05

* Stone Ochre.

Oil	24·5
Water of combination	3·3
Oxide of iron	11·2
Alumina	4·6
Lime salts, etc.	1·2
Insoluble siliceous matter	55·2
	100·0

The variation in composition of these samples, of which those marked with an asterisk (*) were ground in oil, is very remarkable considering that the variation of tint is not great. The large amounts of barium sulphate present in some of these may be naturally occurring, but have probably been added to a natural earth of full colour which would bear lowering. The variations in the amount of ferric oxide, or rather hydroxide, are equally remarkable.

Red ochre was also known to the Greek painters, who obtained it from Cappadocia and called it sinopis; it was also known as rubrica, and now goes under a variety of names as red hæmatite, ruddle, reddle, red chalk, bole, red-iron ore, scarlet ochre, siniped miltos, terra rosa. Its colour is due to anhydrous ferric oxide. A very remarkable feature about this and other red oxide paints is the fact that the proportion of ferric oxide is no indication of the depth of colour, or, rather, affords but slight indication. Church quotes a hæmatite from Cumberland which gave—

Ferric oxide	94·7
Alumina	2·0
Silica	2·2
Moisture	1·1
	100·0

Other "almost equally rich red ochres contain much less iron oxide, a sinopis from Anatolia, analysed by Klaproth, having been found to contain 21 per cent. only, and others from other localities not above 40".

Four samples of Cornish ochres were examined by us with the following results:—

Ferric oxide	40·2	52·3	68·0	85·9
Manganese dioxide	0·8	1·2	1·4	0·6
Lime salts, etc.	4·4	4·6	6·2	4·1
Siliceous matter	54·6	41·9	24·4	9·4
	100·0	100·0	100·0	100·0

These were of a fine colour, but those containing more than traces of manganese were somewhat of a reddish-brown tinge instead of pure red.

Closely allied to red ochre are genuine Indian red and Venetian red.

INDIAN RED should be a natural iron ore or hæmatite containing over 90 per cent. of ferric oxide, and of a rich purplish-red colour. Some of the red imported from India is obtained by roasting lighter-coloured ores, but most specimens are really natural ores. Church states that some is imported from Ormuz in the Persian Gulf, and that some is an English hæmatite from the Forest of Dean. The principal feature, from the colour point of view, of this pigment is the slight purplish tint it possesses.

Indian red as sold is often an admixture of iron oxide with other materials, probably the result of judicious blending of purple brown, red ochre or "light red," and cheap white substances. We give below the composition of samples of the pigment, both in the dry state and ground in oil, which have been examined by us :—

	I.	II.	III.	IV.	V.	VI.
Loss on ignition .	—	22·29	—	30·12	0·75	14·00
Oxide of iron . .	94·00	71·34	96·07	61·92	59·28	53·75
Alumina . . .	1·88	5·26	3·88	6·34	—	
Lime salts, etc. .	3·42				1·15	28·21
Insoluble in H Cl .	0·70	1·11	0·05	1·62	38·82[1]	4·04
	100·00	100·00	100·00	100·00	100·00	100·00

[1] 35·82 per cent. $BaSO_4$.

The two latter samples certainly were not entitled to the name of Indian red, but the others, of which II. and IV. were ground in oil, would appear to be genuine. The adulterated samples seldom have the soft appearance of the genuine Indian red.

VENETIAN RED (Rouge, crocus, colcothar, caput mortuum

vitrioli) originally was a similar produce to Indian red, but of a purer red tone. Of late years various artificially calcined iron oxides and mixed colours—diluted ferric oxides—have been sold under this name.

The following three samples sold as Venetian red were very satisfactory colours, but could hardly be described as hæmatites, or even as calcined iron oxides :—

Loss on ignition	1·50	(including oil)	19·49
Oxide of iron	21·75	17·20	24·42
Alumina	5·00	2·11	
Calcium salts, etc.	11·56	64·94	13·20
Insoluble in hydrochloric acid [1] .	60·19	15 75	42·89
	100·00	100·00	100·00

[1] This was barium sulphate.

We find, in fact, on looking over many analyses, that we have not, in the case of pigments used on the large scale, come across one sample which could be justly termed a hæmatite.

Judging from one of its early names, *caput mortuum vitrioli*, it would appear that calcined green vitriol, or ferrous sulphate, the residue (caput mortuum of the alchemists) of the preparation of Nordhausen sulphuric acid, was recognised as a substitute for the true red earth sold in Venice, or, probably, used by the Venetian school of painters.

Artificial oxides obtained in this and other ways will be considered in a later section of this chapter.

Siennas and Umbers.

These beautiful yellow and brown earths, doubtless, originally took their name from the localities in which they were first found. The existence at Sienna and Umbria of early schools of painters naturally led to the search for suitable colours, and in the ferruginous clay of these districts useful colours were found. The terms now have a more

extended use, and are applied to any earths having the same general properties as those found in Sienna and Umbria. A very valued variety of umber, for instance, comes from Cyprus, and is known as Turkey umber.

Raw Sienna is usually a marl, occasionally a pure, or nearly pure, clay, containing a considerable proportion of ferric hydroxide, or rather, perhaps, hydrated ferric silicate. It is a rather transparent colour, and works well in both water and oil. Its usual tint is a dullish yellow or yellowish-brown, somewhat like the real *khaki*. Its permanence under all ordinarily possible conditions is absolute.

We give below the composition of some samples of this pigment, both in the dry state and ground in water and oil, which have been examined by us :—

DRY SIENNA.

Hygroscopic water	—	—		4·94
Water of combination	11·7	9·30		2·34
Oxide of iron	36·1	30·72		30·18
Alumina			38·83	4·65
Lime salts	33·1			35·64
Insoluble siliceous matter	19·1	21·15		22·25
	100·0	100·00		100·00

SIENNA GROUND IN WATER.

Water	44·70	44·66	42·27	47·59
Water of combination	3·90		3·28	3·09
Oxide of iron	20·44	25·29	18·80	16·02
Alumina			24·30	2·64
Lime salts	17·58	21·05		19·02
Insoluble siliceous matter	13·33	9·00	11·35	11·64
	100·00	100·00	100·00	100·00

RAW SIENNA GROUND IN OIL.

Oil, water of hydration, etc.	40·61	43·12	54·15	34·39	24·3
Oxide of iron	27·89	25·73	31·63	14·20	30·3
Alumina				25·07	7·3
Lime salts	18·98	18·11	6·29		2·9
Insoluble siliceous matter	12·52	13·04	7·93	26·34	35·2
	100·00	100·00	100·00	100·00	100·0

It will be noticed that, speaking generally, the proportion of siliceous matter is much lower in these earths than in the ochres. Those ochres which contain only a small amount of silica are usually of a deeper, browner shade, more approaching these colours. In fact, the difference between yellow ochre and raw sienna would appear to be rather one of locality and depth of tint than of constitution, of degree rather than kind.

Burnt Sienna is, or should be, obtained by carefully calcining raw sienna, until, by the expulsion of a portion or the whole of the water of combination, a rich reddish-brown pigment is obtained. This, like raw sienna, works well in both oil and water, and from its pleasing colour and great permanency is held in considerable esteem. Judging from the composition of some samples we have examined, we think it probable that any ferruginous earth of the requisite reddish-brown shade is sold as burnt sienna. This substitution cannot altogether be regarded as fraudulent, as it is difficult to see in what way the buyer is injured, provided the tint is right and permanent.

The small amount of lime in some of these siennas is very remarkable, and rather tends to support the opinion expressed above as to substitution of any suitably coloured earth.

We give the composition of samples of this pigment examined by us :—

BURNT SIENNA GROUND IN WATER.

Water (loss at 100°)	43·80	47·59
Water of combination	2·47	1·59
Oxide of iron	30·42	25·69
Alumina	7·90	4·92
Lime salts		7·07
Insoluble siliceous matter	15·41	13·14
	100·00	100·00

BURNT SIENNA GROUND IN OIL.

Oil	41·08	50·07	37·9	56·5
Water of combination, etc.	—	—	3·7	7·8
Oxide of iron	22·83	29·47	11·9	22·6
Alumina	10·34	4·83	0·7	1·3
Lime salts		1·84	0·6	—
Insoluble siliceous matter	25·75	13·79	7·8	12·6
Barium Sulphate	—	—	37·4	—
	100·00	100·00	100·0	100·8

Raw Umber (*Levant umber, Turkey umber, Terra 'Ombre, umbraun, umbra, Kölnische Erde, Terra Ombra*).—This brown earth, most of which comes from Cyprus, owes its olive brown colour, in which it differs from most of the iron colours, to the presence of a considerable quantity of oxides of manganese. An analysis by Church of a choice sample of Cyprus umber will indicate the general character of this pigment :—

Water given off at 100° C.	4·8
Water given off at a red heat	8·8
Iron oxide	48·5
Manganese dioxide	19·0
Lime	1·4
Magnesia	0·5
Alumina	2·1
Phosphoric acid	0·9
Silica	13·7
Carbonic acid, etc.	0·3
	100·0

Prof. Church remarks that "this sample had the peculiar greenish hue so much prized by artists," and that "it should be stated that a part of the manganese probably existed as Mn_3O_4".

The pigment is prepared by levigation, and subsequent drying at a temperature not much exceeding 100° C. If this is exceeded, not only will the hygroscopic moisture be expelled, but some of the water of combination, and a more or less burnt umber will result.

Raw umber is a very valuable pigment, as its colour is not easy to satisfactorily imitate, and it is under all ordinary conditions quite permanent: any changes in colour are more probably due to yellowing of the oil used as a vehicle than to alteration in the colour itself; slight changes are also occasionally noticed in water colour, probably attributable to the use of a slightly bituminous earth, but in neither case is the change serious.

We give below the composition of samples of raw umber obtained from various sources and examined by us :—

	I. High class artists' colour in oil.	II. Oil-free Matter of I.	III. Turkey Umber.	IV. English Umber.	V. Prepared Umber.	
Oil	47·6	—	—	—	—	
Moisture	7·7	14·6	4·3	12·6	5·2	
Water of combination			6·9	8·3	11·0	
Ferric oxide	18·5	35·1	44·9	47·1	50·4	Fe_2O_3 & Al_2O_3 not separated
Manganese dioxide	11·2	21·3	14·0	10·5	13·8	
Alumina	1·8	3·4	5·8	3·1	—	
Lime salts, etc.	4·5	9·1	4·8	3·0	3·6	
Insoluble siliceous matter	8·7	16·5	19·3	15·4	16·0	
	100·0	100·0	100·0	100·0	100·0	

The percentage of manganese is, it will be noted, highest in the artists' colour and lowest in the English umber. We are not aware what process the prepared umber had passed through, but judging from its composition and colour we feel justified in stating that it had not been ignited ("burnt").

Burnt Umber, as its name implies, is obtained by calcining the earth known as raw umber. It is slightly redder and darker than the unburnt earth, the change being due to some alteration in the hydration and constitution of the oxides of iron and manganese present. Prof. Church justly remarks that if the iron were present in umber to any considerable extent as ordinary hydroxides a much redder product should be obtained on calcination than is actually the case. Burnt umber is more translucent than the raw earth, and is to all

intents and purposes absolutely permanent and inert to other pigments.

We give some analytical figures which will sufficiently indicate the composition of this colour:—

	Burnt Turkey Umber.	Burnt Umber.
Moisture	2·5	6·00
Water of combination, etc.	4·2	—
Ferric oxide	45·9	46·50
Oxide of manganese	15·6	9·40
Alumina	2·5	—[1]
Lime salts, etc.	3·8	16·85
Insoluble siliceous matter	25·5	21·25
	100·0	100·00

[1] Included with the ferric oxide.

BURNT UMBER IN OIL.

		Burnt Turkey Umber.	
Oil, Water of combination, etc.	39·7	45·1	32·8
Ferric oxide	22·8	26·7	18·6
Oxide of manganese	4·3	9·0	6·8
Alumina	3·9	3·4	1·3
Lime salts	11·2	3·4	0·3
Insoluble siliceous matter[1]	18·1	12·4	40 2
	100·0	100·0	100·0

[1] And $BaSO_4$ 10·5 per cent., 2·5 per cent., 30·4 per cent.

The samples poor in manganese and containing barium sulphate in quantity were probably not genuine Turkey umber, but of English or Continental origin. They are seldom as fine in colour as the real Turkey (Cyprus) earth and are not by any means as costly or highly esteemed.

Light Red, a colour more in use for artistic than for utilitarian purposes, is, when genuine, a prepared ochre, a roasted yellow ochre. It is usually lighter and brighter than red ochre; Church well defines its colour as scarlet, modified by a little yellow and grey.

The colour of light red is obviously due to anhydrous

ferric oxide, and to obtain a good colour an ochre free from organic matter, which is not easy to burn off without heating beyond the temperature required for a bright red, and one not too rich in lime, should be used. The temperature of roasting should not be too high; a dull, red heat is sufficient. It must be remembered that ferric oxide colours look very much darker when hot than after cooling. The product is thrown into cold water, ground and washed.

Light red is used in both oil and water-colour painting, and is quite permanent. We give the composition of two samples of this pigment ground in oil and sold by artists' colourmen of repute, examined by us:—

	I.	II.
Oil	51·6	43·9
Water of combination		
Ferric oxide	6·0	22·8
Alumina	3·8	5·7
Lime salts, etc.	2·6	1·0
Barium sulphate.	3·5	—
Insoluble siliceous matter	32·5	26·6
	100·0	100·0

The difference in the percentage of ferric oxide is very remarkable, and, as the colours were of very similar tint, shows how little colour depends on the amount of iron and how much on its condition. Both samples might have been and probably were obtained by calcining natural earths, the small amount of barium sulphate present in I. being present either as a natural or accidental ingredient of the earth, or possibly added to reduce the pigment to a standard tint.

Cappagh Brown (*Euchrome—Mineral Brown*).—This brown earth, which in most respects resembles umber but is more reddish, is found in the Cappagh mines on the estate of Lord Audley near Skibbereen in Co. Cork. It gives off a good deal of water at 100° and contains only traces of organic matter. An analysis by Church is given below:—

Water, given off at 100° C.	18·7
Water, given off at a red heat	11·6
Ferric oxide (Fe_2O_3)	34·4
Manganese dioxide (MnO_2)	27·2
Alumina	2·6
Lime	1·1
Magnesia	trace
Silica	4·6
Phosphoric acid	0·4
	100·6

Prof. Church states that probably some of the manganese exists as red oxide (Mn_3O_4) and also, very sensibly, suggests that "the large quantity of water present in this mineral in a loosely attached form (hygroscopic), amounting to nearly one-fifth of the weight of the pigment indicates the the desirability of cautiously drying the substance previous to grinding it in oil. A temperature of 60° C. should not be exceeded."

Cappagh brown works well in oil, particularly if dried as suggested. Church found that it became slightly redder on exposure for one month to light, but the change did not appear to increase after a further five months' exposure.

Red Oxide (*Chocolate, Purple Brown, etc.*).

For rough outdoor work, the protection of ironwork and other purposes where it is desirable to obtain a cheap protective coating rather than a particularly rich or delicate colour, coarse natural oxides are ground first roughly and then to a fine powder and used, ground in oil, under the name of red oxide, red oxide of iron, oxide, chocolate, etc. Those called red oxide of iron are usually fairly pure, but the others frequently contain considerable quantities of barium sulphate, sometimes natural, sometimes added. The colours of these oxides vary from a dark chocolate to a dull brickish red.

These natural oxides and their artificial allies are very

much used for painting bridges, girders and all sorts of iron structures. So long as the oil with which these materials are incorporated retains its tenacity and imperviousness to water such coatings will be protective to ironwork, but when water is able to make its way to the iron surface it seems only too probable that the presence of iron oxide in the paint is likely to cause corrosion by acting as the electro-negative element in a couple, in the same way as a spot of rust on the bright blade of a knife or razor will, if not rubbed off, grow over the whole blade.

The artificial oxide reds are prepared by the calcination of copperas (ferrous sulphate), or by the precipitation of ferric oxide by means of milk of lime or alkaline solutions from waste iron liquors. The shade of those produced by ignition varies according to the temperature and time of roasting, from a light red to a purple. The shade of colour is also regulated by the presence (either added or naturally) of more or less lime salts, or barium sulphate. It is remarkable how little the shade of these colours seems to depend on the amount of iron present, the physical changes produced by roasting having apparently far more effect.

Below we give the composition of iron-oxide colours of various shades, some dry, some ground in oil :—

RED OXIDES.

	I.	II.	III.
Oil	—	—	12·3
Water of combination	0·4	0·6	—
Ferric oxide	90·5	96·7	22·5
Alumina	—	—	—
Lime salts, etc.	2·5	traces	23·6
Insoluble siliceous matter	6·6	2·7	5·2
Barium sulphate	—	—	36·4
	100·0	100·0	100·0

PURPLE AND CHOCOLATE.

	Light Purple Brown.	Middle Purple Brown.	Dark Purple Brown.				Purple.	Chocolate.	
	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
Oil	22·6	—	—	—	14·0	14·6	10·0	—	—
Water of combination	—	0·5	—	—	—	—	—	—	—
Ferric oxide	57·2	93·6	97·4	85·4	84·1	80·7	18·4	97·8	90·0
Alumina	—	2·9	—	7·4	—	—	—	—	5·3
Lime salts, etc.	2·1	—	·6		—	3·2	·3	·4	1·0
Insol. siliceous matter	18·1	3·0	2·0	7·2	1·9	1·5	5·7	1·8	3·7
Barium sulphate	—	—	—	—	—	—	65·6	—	—
	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0	100·0

The difference in composition of similarly coloured materials, and the similarity in composition of differently coloured materials, are well illustrated in these examples. Compare I. and II. with III.; X. with any of the other purples; II. with VI.

The darker shades of colours, purple and chocolate, are obtained by strongly igniting the red oxides, the higher the temperature of ignition the deeper and more violet is the colour obtained.

Mars Colours.

The Mars colours are a series of artificial oxide of iron colours prepared by precipitating ferrous sulphate with milk of lime, drying the resulting mixed precipitate of ferrous hydroxide and calcium sulphate in the air—when the ferrous hydroxide becomes oxidised to the ferric compound—and roasting or strongly igniting; according to the temperature, a yellow, orange or brown pigment is obtained. These colours, like all the ferric oxide colours, are absolutely permanent.

Terre Verte (*Green Verona Earth*).

This natural green pigment is found at Verona, in Italy, and at Cyprus. It is extremely permanent, and owes its

colour to the presence of ferrous oxide, probably combined as a silicate. We give the composition of two samples examined by some rather ancient authorities:—

	Berthier or Delesse. Verona.	Klaproth. Cyprus.
Silica	51·21	51·5
Alumina	7·25	—
Ferrous oxide	20·72	20·5
Magnesia	6·16	1·5
Soda	6·21	—
Potash	—	18·0
Water	4·49	8·0
Manganese oxide	trace	—
	96·04	99·5

These analyses are not very satisfactory, but both seem to indicate that the substance is a ferrous alkaline silicate. The presence of soda and magnesia in the Verona sample, and of potash with only a small quantity of magnesia in that from Cyprus, is of interest.

The Veronese earth is usually of a purer green than that from Cyprus, which is of a verdigris to apple-green colour.

Prussian Brown.

This colour, which is not used to any great extent, is prepared by the careful ignition of Prussian blue. It consists almost entirely of ferric oxide. Prussian blue on ignition gives off cyanogen and apparently leaves a residue of metallic iron which, being in an extremely fine state of division, readily burns, becoming red hot, to a brown oxide of iron. Should the temperature become too high the product is too dark. As Prussian blue is never pure ferric ferrocyanide but always contains alkali-iron cyanide and usually other alkaline salts, it is, even when using genuine samples of blue, not always easy to ensure regularity of tint in the brown pigment. This brown can be diluted to shade by means of the ever-useful barytes or other white pigments.

The analysis of the iron oxide pigments does not present very great difficulties. In the case of red and yellow pigments the following method of procedure should be adopted. A suitable amount, say 1 to 2 grams, of the dry pigment is weighed in a platinum or porcelain capsule and ignited to a dull red heat. In the case of a dry pigment the loss represents the amount of moisture and water of hydration with, in some cases, traces of organic matter. The residue after ignition is scraped into a beaker and treated with concentrated hydrochloric acid, notice being taken whether effervescence occurs (indicating presence of a carbonate). After standing in the water-bath from half to three-quarters of an hour the contents of the beaker are examined and, if the insoluble residue does not appear reddish, diluted with water, allowed to stand for any insoluble matter to deposit, and filtered. The residue in the filter is washed, ignited without drying, and weighed. It may be silica or clay, or barium sulphate with one or both of these. Fusion with alkaline carbonates will convert silica into alkaline silicates soluble in water, clay into alkaline silicates and aluminates, and barium sulphate into barium carbonate and alkaline sulphates. It is usually only desirable to determine the amount of barium, which, being usually weighed as sulphate and occurring in pigments in this form, is returned as such.

If the residue from the HCl treatment is coloured it should be re-treated, after weighing, with acid and re-filtered. The filtrate is mixed with the original filtrate and the insoluble matter again weighed. It can then be determined whether a further treatment is necessary or not. The whole of the filtrate and washings is diluted to 250, 500, or 1,000 c.c., according to circumstances, and a convenient aliquot part, say $\frac{1}{5}$, taken, diluted if necessary, and ammonia, in slight excess, added. The liquid is heated to boiling to expel the excess of ammonia. The precipitate is washed once or twice by

decantation, transferred to the filter and allowed to drain. It is then re-transferred to the beaker, re-dissolved in large excess of hydrochloric acid, suitably diluted and re-precipitated with ammonia. By this means any co-precipitated lime is removed and a precipitate consisting only of ferric oxide and alumina (with possible traces of P_2O_5 and Cr_2O_3) obtained. This is weighed. The iron can be determined in another portion of the original liquid by titration with $\frac{N}{10}$ $K_2Cr_2O_7$ after reduction or in the redissolved weighed ammonia precipitate. The former is the more expeditious method. The filtrate from the "ammonia precipitate" contains the lime, magnesia, etc. These may be determined or not as desired. The hygroscopic moisture should be determined in a separate portion in a water oven at 100°.

In the case of pigments ground in oil it is usually sufficient to determine the total loss on ignition, and not to determine the actual percentage of oil, though, of course, for scientific purposes it is certainly better to do this. The determination can be effected in the manner described under "white lead".

The brown pigments present rather more difficulty, as many of them contain manganese. The best method, in this case, is to, in the original (filtered) hydrochloric acid solution, adopt the method of separation based on the behaviour of the acetates of iron and alumina on heating. The hydrochloric acid solution is nearly neutralised with ammonia, care being taken, however, to leave a slight amount of free acid, and then a saturated solution of sodium acetate added in sufficiency to be in slight excess. The liquid, which was yellow, becomes of a deep red colour, owing to the formation of ferric acetate, and smells of acetic acid. This liquid on boiling becomes turbid and deposits a flocculent precipitate of basic ferric (and aluminic) acetate. The manganese remains in solution. The basic ferric acetate (or mixed acetates as the case may be) is collected and washed; in very accurate

analyses, Fresenius recommends re-solution and precipitation, but this is not usually at all necessary: the precipitate is then dried, ignited, and re-dissolved in HCl, precipitated by ammonia as hydroxide, collected, weighed, and the amount of iron determined by titration, after reduction, with $\frac{N}{10}$ $K_2Cr_2O_7$. By this means the percentages of iron oxide and alumina can be determined. In the filtrate from the basic acetates manganese can be determined by making alkaline with ammonia, with the addition of ammonium chloride, and either passing sulphuretted hydrogen or adding ammonium sulphide. Manganese is precipitated as sulphide.[1] The precipitate is collected, washed, and weighed, either as sulphide after ignition with sulphur in a current of H_2S, or re-dissolved in HCl and precipitated by Na_2CO_3 as $MnCO_3$, which on ignition becomes Mn_3O_4. The filtrate from the manganese may contain lime, magnesia, etc. Ammonium oxalate, in slightly acetic solution, will precipitate the lime, which can be weighed as carbonate or oxide, and the filtrate, after concentration, can be treated with ammonia and sodium or ammonium phosphate to precipitate the magnesia as $MgNH_4PO_4$, which on careful ignition becomes $Mg_2P_2O_7$; but this is seldom necessary.

VI.—COBALT COLOURS.

The metal cobalt enters into the composition of some few colours, in each case as the chromogenic constituent. These cobalt colours may be considered as of three kinds: (*a*) pigments formed of a white basic oxide with cobalt oxide; (*b*)

[1] It is desirable that a considerable quantity of ammonium chloride should be present in the solution from which manganese sulphide is to be precipitated, and that the solution should stand twenty-four hours after the addition of ammonium sulphide before filtering. The sulphide should be washed with water containing ammonium sulphide, and the funnel not allowed to remain empty after each washing runs through, as otherwise oxidation may occur, and manganese pass through the filter.

silicate of cobalt; (*c*) cobalt potassium nitrite. We will consider these three classes.

(a) Cobalt Oxide with a Basic Oxide.

Cobalt Blue (*Cobalt Ultramarine, Thénard's Blue*).—Cobalt blue is, according to its method of preparation, a mixture of either oxide, phosphate or arsenate of cobalt with alumina, and is a fine deep blue, somewhat like ultramarine, but with a tendency to violet which is more marked in artificial light. It is prepared by precipitating a solution of a cobalt salt (the nitrate, acetate or chloride) with sodium phosphate or arsenate. The gelatinous violet precipitate thus obtained is washed well with water and mixed with three to five times its volume (or more in the case of the arsenate) of freshly precipitated and washed alumina. The mixture is thoroughly incorporated and dried until brittle and in a suitable condition for ignition. It is then transferred to a clay crucible, which is well covered and ignited to a cherry red for about half an hour. It is important that no reducing gases should be allowed access to the ignited mass, and Regnault has suggested the addition of a small quantity of mercuric oxide which gives off oxygen on heating, and the mercury volatilising leaves no residue to contaminate the product. It is important that the cobalt salt and the alumina used should be free from all other metals, the oxides of which are coloured, *e.g.*, iron nickel, manganese.

Another process by which a similar but inferior colour is obtained is, the co-precipitation of the oxides of cobalt and aluminium from a mixture of the salts, *e.g.*, cobalt nitrate and alum, by means of sodium carbonate. The precipitate of mixed oxides is washed, dried and ignited as is, in the former method, the mixed phosphate or arsenate and alumina.

Binden recommends that cobalt chloride should be treated

with ammonia to precipitate the oxide, which, after washing, is mixed with alumina and ignited.

Cobalt blue is permanent, non-poisonous and a fine colour, though, as already stated, somewhat inclined to violet. It lacks the brilliance of ultramarine, which as a blue is unsurpassed.

Cobalt Pink.—This pigment is prepared by mixing magnesium carbonate and a solution of cobaltous nitrate to a paste and calcining the mixture, after evaporation to dryness, in a covered crucible.

Cobalt Brown.—A brown pigment is prepared by adding ferric oxide to the mixture of alumina and cobalt salt used for making the blue, or by igniting ammonia alum with cobalt sulphate and ferrous sulphate; a high temperature is requisite for the carrying out of this latter process.

These cobalt-basic-oxide compounds, from the fact that the presence of reducing gases in the crucible damages the pigment, and that the addition of mercuric oxide or manganese dioxide tends to improve the pigment, would appear to be cobaltic compounds.

Another pigment which to some extent belongs to this class is

Cœruleum (*Cœlin*, *Bleu Céleste*).

This pigment, which is lighter in colour than cobalt blue, is apparently a stannate of cobalt, mixed with calcium sulphate and silica. It is said to be in a state of purity,

$$3\,(SnO_2CoO) + SnO_2.$$

An analysis given by an unknown authority is as follows:—

Stannic oxide	49·66
Cobaltous oxide	18·66
Calcium sulphate and silica	31·68
	100·00

Cobalt Green (*Rinmann's Green*).—When cobalt oxide is

ignited with oxide of zinc instead of oxide of aluminium, a green colour is obtained; this fact is well known to those who are accustomed to blow-pipe analysis.

This cobalt green is prepared by precipitating from a pure cobalt salt in solution (10 per cent.) the phosphate or arsenate, and, after washing, mixing the precipitate with zinc oxide, and igniting. Sodium carbonate may, less satisfactorily, be substituted for sodium phosphate or arsenate, or a mixed solution of zinc sulphate and cobalt nitrate may be precipitated by sodium carbonate. Another method is to mix a solution of a cobalt salt with zinc oxide, evaporate to dryness and ignite.

Some analyses of this pigment are given by R. Wagner. One from the University of Würzburg had the following composition :—

Zinc oxide	88·040
Ferric oxide	0·298
Cobaltous oxide	11·662
	100·000

This was a light green.

Two samples prepared by himself agreed more with what might be expected from the former mode of preparation described by us :—

Zinc oxide	71·93	71·68
Cobaltous oxide	19·15	18·93
Phosphoric anhydride	8·22	8·29
Sodium oxide	0·69	—
	99·99	98·90

The sodium oxide was probably present as an impurity due to imperfect washing.

(b) Cobalt Silicates.

Smalt (*Bleu d'azur, Bleu de Saxe—Saxon blue*).—Smalt is a blue colour prepared in Saxony and in Norway, in the

former country usually from *smaltine* (smaltite), an analysis of which by Hofmann is given below:—

SMALTINE FROM SCHNEEBERG.

Arsenic	70·37
Cobalt	13·95
Nickel	1·79
Iron	11·71
Copper	1·39
Sulphur	0·66
Bismuth	0·01
	99·88

The typical kind is (Co, Fe, Ni) As_2.

In Norway *cobaltite* CoAsS (or $CoS_2 + CoAs_2$) is the ore used.

Smalt is a silicate of cobalt and potassium, and is prepared by fusing a crude cobalt oxide with potassium carbonate and quartz. The process is conducted in several stages.

The ore is first carefully selected and all casual impurities rejected, and is then placed in charges of about three cwt. in a layer five or six inches thick, on the bed of a reverberatory furnace or in a muffle, the object being to roast it in a current of air. By this means the sulphur and a great part of the arsenic is expelled as SO_2 and As_2O_3 respectively, the latter oxide being collected in condensing chambers. The roasting should be continued until only sufficient arsenic is left to combine with the less oxidisable metals, the cobalt being converted into oxide. Test portions are taken out from time to time until the tint of the glass obtained is satisfactory, when the roasting is stopped.

Pure quartz ignited, then slaked and crushed, is washed by levigation from any iron oxide or other impurities. This is mixed with pure potassium carbonate, about one part of the latter being used for three parts of roasted ore and the same quantity of quartz, and some arsenious oxide added to oxidise any ferrous oxide present. The exact amount of

these ingredients required is ascertained by making small tests.

Very refractory melting pots are used and placed in a furnace similar to that of a glass oven. This is raised to a very high temperature and in about eight hours the mass fuses. It is from time to time stirred to thoroughly mix and to break up any crust which may form on the surface of the melt. At a white heat the cobalt oxide begins to be attacked by the silicate and a blue glass is formed. The mixed arsenides of the other metals with some cobalt sink to the bottom of the pot and form a brittle metallic-looking speiss. The mass is left for some time at a white heat to allow this to settle completely and the smalt ladled out into vessels of cold water. An easily pulverised glass is thus obtained. The *speiss*, which begins to be scooped up with the smalt as the bottom of the vessel is neared, is more fusible and may be poured out from under the blue into a niche connected with the furnace chimney, thus allowing the fumes of arsenic to escape.

The glass is now crushed, ground fine and levigated. As it is a more or less transparent substance the portions of medium fineness are more suitable for colouring purposes than the very finely ground portions, which must be re-smelted.

The presence of other oxides than those of cobalt and potassium is prejudicial to the colour of the product; baryta gives a deep indigo tint, sodium, calcium and magnesium produce a reddish shade, iron a blackish green, manganese violet, nickel a less intense violet; copper, zinc, bismuth and antimony give dull shades.

The composition of three samples of smalt examined by Ludwig (from *Thorpe's Dictionary*) is given below :—

	Norwegian deep-coloured sample.	German deep coloured.	German pale coarse.
Silica	70·86	66·20	72·12
Potash and soda	21·41	16·31	20·04
Cobaltous oxide	6·49	6·75	1·95
Alumina	0·43	8·64	1·80
Protoxide of iron	0·24	1·36	1·40
Arsenious acid	trace	—	0·08
Water and carbonic acid	0·57	0·92	0·46
	100·00	100·18[1]	97·85

(c) Aureolin (*Potassio Cobaltic Nitrite*).

This deep lemon-yellow pigment is prepared by adding potassium nitrite to a cobaltous solution acidified with acetic acid. Nitrogen is set free and the salt separates as a yellow crystalline powder—

$$Co_2 (NO_2)_6 \, 6KNO_2 + nH_2O.$$

It is desirable to use strong solutions, as otherwise relatively large crystals are formed and the pigment has little covering power.

Aureolin, sometimes called Indian yellow, is a very permanent yellow, but from the nature of its constituents is expensive and only suitable for artists' use. It works well in both oil and water. It is quite a modern colour.

VII.—COPPER PIGMENTS.

Copper Greens.

The hydrated and some other compounds of copper are, as is well known, usually of a blue or green colour, and some of these have from very early ages been used as green colours. The compounds principally used are the basic carbonate, the basic acetate, and the arsenite and aceto-arsenite; the basic chloride was also formerly used under the

[1] This total is given in the *Dictionary* as 101·18.

name of Brunswick green, which name is now applied to Prussian blue green, a chromate. We will consider these colours individually.

MALACHITE (*Basic Carbonate of Copper, Green Verditer, Green Bice, Mountain Green—Vert de Montagne, Berggrün*).—This pigment is the most ancient of all the copper greens; Sir H. Davy in his researches on the pigments found in the baths of Titus and Flavia and other ruins at Rome and Pompeii found this pigment used for mural decoration.

Malachite is a mineral found in various localities in Europe, Africa, America and Australia. The following list is from Dana: The Urals; at Chessy in France; at Schwatz in the Tyrol; in Cornwall and in Cumberland; Sandlodge Copper Mine in Scotland; Limerick, Waterford and elsewhere in Ireland; at Grimberg, near Siegen, in Germany; at the copper mines of Nischne Tagilsk; at Bembe on the west coast of Africa; with the copper ores of Cuba, Chili, Australia, and in New Jersey, Pennsylvania, Winsconsin and California.

The mineral which is highly valued for ornamental purposes is named from *μαλαχή, mallows*, in allusion to its green colour; and its composition corresponds to $CuCO_3$ $Cu(OH)_2$. This corresponds to

CO_2	19·9
CuO	71·9
H_2O	8·2
	100·0

Malachite only requires careful selection of pure pieces—free from ochreous matter, and grinding to render it fit for use as a pigment.

Church states that "Malachite as an oil paint has often proved to be permanent, although it may seem to acquire a dull, brownish hue, owing to the darkening and yellowing

of the oil; sometimes, however, it becomes somewhat olive in colour".

Various artificial preparations have from time to time been proposed in place of this very expensive mineral for use as pigments. We give in the next sections a description of the preparation of some of these and of similar blue substances.

Bremen Green (*Green Verditer*).—This colour, which is now but little used except, we believe, by artists and paper stainers, consists chiefly of basic carbonate of copper, mixed with alumina and calcium carbonate. According to Bley, a fine blue-green colour is obtained by dissolving copper sulphate in 10 parts of water, adding a little nitric acid, leaving the solution to itself for a week, then filtering, adding fresh lime water, precipitating with filtered solution of pearl ash and mixing the washed product with gum water to give it lustre (Watt's *Dictionary of Chemistry*). The object of adding nitric acid is to prevent precipitation of copper carbonate by the lime salts in the water used for solution, and the prolonged keeping of the solution facilitates the precipitation of any insoluble impurities. Another action of nitric acid would be to oxidise any ferrous salts present as impurities, which means that any precipitate due to iron is yellow ferric hydroxide, which is permanent, and not greenish ferrous hydroxide, which will become yellow.

At Bremen and Cassel this pigment is, according to Gentele, prepared by grinding 225 lb. of sea salt with 222 lb. of crystallised copper sulphate and water to a thick paste. With this, 225 lb. sheet copper, cut into pieces about 1 in. square, is mixed in strata in a wooden chest made without nails, and digested for three months, with stirring about once a week. At the end of this period the undissolved metal is removed and the precipitate washed with the minimum amount of water. One hundred and eighty pounds of this

is thrown into a tub with 12 lb. of hydrochloric acid of 13° Baumé, well stirred and left for twenty-four to thirty hours; to 6 volumes of this, 15 volumes of sodium hydroxide (19° Baumé) and afterwards 6 volumes of water are added. The precipitate is washed, filtered, exposed to the air, and dried.

Another method, described by Habich, is to treat copper sheathing with about equal parts of potassium sulphate and sodium chloride, forming a paste of the mixture and stirring for some months, or to treat 100 parts of copper with 60 parts of salt and 30 parts of sulphuric acid diluted with three times its volume of water, exposing for some time to the fresh air, and in either case to treat the magma (100 kilos) with copper sulphate (7 kilos) and concentrated soda solution (40 kilos); then stir vigorously and pour into 150 kilos of sodium hydroxide (20° Baumé) wash, pass through hair sieves and dry at a temperature not above 78° F.

In these processes, which appear to be unnecessarily complicated, it would seem that under the influence of air and hydrochloric acid, or air and alkaline chloride, copper becomes converted into basic chloride or copper oxy-chloride, which is then converted into an hydroxide which may or may not be allowed to carbonate.

In the process described by Gentele it is conceivable that a double decomposition occurs thus :—

$$CuSO_4 + 2\,NaCl = CuCl_2 + Na_2SO_4,$$

cupric chloride acting on copper forms cuprous chloride—

$$CuCl_2 + Cu = Cu_2Cl_2.$$

This, on oxidation, may become an oxy-chloride—

$$Cu_2Cl_2 + O = CuCl_2\,CuO.$$

The object of adding hydrochloric acid to this is difficult to see, and the addition of caustic soda should result in the formation of cupric hydroxide and not carbonate. Unless it is the case

that a certain amount of oxy-chloride is left in the colour it is most difficult to understand why such complicated processes are used apparently only to produce cupric hydroxide.

Scheele's Green (*Cupric Arsenite, Swedish Green, Mittis Green, Scheele's Grün, Vienna Green, Veronese Green*).—This pigment, discovered by Scheele in 1778 is an arsenite of copper containing an excess of copper oxide, prepared by precipitation. Scheele's original process was to dissolve 1 part of arsenious anhydride and 2 parts of potassium carbonate by boiling in 35 parts of water, filtering if necessary, and adding until no further precipitation occurs to a solution of 2 parts of copper sulphate in water. The precipitate was collected, washed and dried at a gentle heat (it will not bear ignition). Church recommends that solutions of arsenious acid and copper sulphate should be mixed and potassium carbonate added until the maximum intensity of colour is obtained. Various other methods have been adopted, but the pigment is not much used now, having become very much discredited owing to its poisonous nature and inferiority to other copper-arsenic compounds. It is a pale but not very bright green and can be readily distinguished from malachite on the one hand and emerald green on the other by giving a reaction with Marsh's test, a sublimate of arsenious acid on heating, and not effervescing with dilute mineral acids (differences from malachite), and by not giving off acetic acid vapours on heating with strong sulphuric acid (difference from emerald green).

Emerald Green (*Cupric Aceto-Arsenite, Schweinfurt Green, Paris Green*).—This pigment, which has now almost superseded Scheele's green, is a most brilliant colour. It is a mixture or compound of arsenate and acetate of copper supposed to correspond to

$$3\,CuO\,As_2O_3\,Cu(C_2H_3O_2)_2.$$

Various methods of preparation are employed, of which the following are of interest.

Five parts of verdigris (basic acetate of copper) made into a thin paste with water are added to a boiling solution of more than 4 parts of arsenic trioxide in 50 parts of water, the solution being kept boiling during the addition, and acetic acid being added if a yellowish-green precipitate separates. On further boiling for a few minutes the precipitate becomes crystalline and of the characteristic bright green colour.

Boiling concentrated solutions of arsenious oxide and copper acetate are mixed in such proportions that equal weights of the two substances are present, when a bulky olive-green precipitate falls—the liquid is diluted with an equal volume of water and the mixture placed in a flask which is filled to the neck to prevent any pellicle which forms on the surface from falling and starting premature crystallisation.

The colour thus prepared separates out in the course of two or three days and owes, it is supposed, much of its beauty to the gradual nature of its formation.

We give the composition of some samples of emerald green examined by us :—

	Deep.		Light.	
Moisture	—	1·6	—	1·1
Arsenious oxide	56·6	52·7	49·4	46·8
Cupric oxide	35·0	31·5	28·2	26·2
Acetic anhydride, etc . . .	8·4	14·2	14·6	13·1
Insoluble in acid	—	—	7·8	12·8
	100·0	100·0	100·0	100·0

These samples were most brilliant colours; the light greens were "lowered" with barium sulphate.

The ratio of arsenious oxide to cupric oxide in each of these four samples is approximately 2 molecules to 3 molecules. The actual figures work out

1 : 1·55, 1 : 1·50, 1 : 1·44, 1 : 1·40.

The ratio calculated from the formula ascribed to the pure compound is $3As_2O_3 : 4CuO$, and the percentage composition

As_2O_3	58·7
CuO	31·2
$(C_2H_3O)_2O$	10·1
	100·0

The excess of copper found is probably due to the presence of verdigris or other basic-copper compounds.

Emerald green is dissolved by acids without effervescence to a blue or green solution; on warming the solution acetic acid is evolved. Marsh's and Reinsch's tests indicate the presence of arsenic. On ignition it is blackened with evolution of acetous vapours and formation of a white sublimate of arsenious anhydride.

The analysis of the copper-arsenic colours presents no great difficulty. A portion, not more than 1 gram, is treated with hydrochloric acid and nitric acid or potassium chlorate added to oxidise the arsenious to arsenic acid, the liquid diluted, and, if necessary, filtered from any insoluble matter, which should be weighed. The filtrate, in the known absence of lead or other heavy metals, is made strongly alkaline with ammonia and excess of magnesium mixture added. Magnesium ammonium arsenate forms, and after some hours standing, with frequent stirring, precipitation is complete. The precipitate is filtered off and washed, until free from dissolved matter, with dilute ammonia. The magnesium ammonium arsenate may be weighed as such after very long drying at 105° C. or, better, is slowly ignited at a gradually increasing temperature until all NH_3 is expelled, and the residual magnesium pyroarsenate $Mg_2As_2O_7$ weighed. The filtrate from the arsenic contains all the copper as blue ammonio-cupric salt. This is concentrated and acidulated with hydrochloric or sulphuric acid, transferred to a weighed platinum dish and zinc added. The copper is precipitated

on the platinum and when all the zinc is dissolved, and the liquid carefully poured off, the spongy copper is pressed together and washed repeatedly with hot water, then with alcohol, and lastly with ether. This should be done quickly and the dish dried in the water oven. The increase in weight gives the weight of copper present in the amount of green taken. The supernatant liquid from this operation should be tested with a fresh piece of zinc and a few drops of acid, for any copper not precipitated. If carefully carried out this process is very accurate; excess of zinc is necessary to precipitate all the copper and excess of acid to dissolve all the zinc. A test with zinc and acid alone should show no residue insoluble in acid; if this is found the zinc is unsuitable for the purpose.

If lead is present it can be removed by precipitation with a large excess of diluted sulphuric acid. The lead sulphate should be washed twice with dilute sulphuric acid to remove arsenic and copper, and then with alcohol to remove sulphuric acid. Any precipitate with ammonia should be filtered off and examined before precipitating the arsenate. Lead chromate, which might be used to lighten the pigment, would, after solution in HCl give a precipitate of chromium arsenate under these conditions.

Verdigris (*Vert de Gris, Grünspan*).—Under the name verdigris several of the acetates of copper are included; those which are of importance as pigments are *blue* verdigris—dibasic cupric acetate, and *green* verdigris—a mixture of di- and tri-basic acetates, or a sesqui-acetate. Blue verdigris is prepared at Montpellier and other parts of France by exposing copper plates to the air in contact with fermenting wine lees or marc. The acetous fermentation sets up, and verdigris forms. The plates are, after about three weeks' action, taken out, placed in an upright position to dry, dipped in water about once a week for six or eight weeks, and the verdigris, which swells up, is scraped off. The plates

are then again treated with wine lees and re-treated until entirely corroded. When the plates are new action is facilitated by brushing them with a solution of normal acetate of copper.

Blue verdigris is also formed by exposing copper plates to damp air in contact with a paste of the normal acetate and water.

It is obvious that, whatever process is used, old corrugated copper plates will give a better yield by reason of the greater surface they present than new bright plates.

Verdigris forms silky blue needles and scales which grind to a beautiful blue powder. It is CuO, $Cu(C_2H_3O_2)_2 + 6H_2O$. On heating to 60° C. the water is given up and a green mixture of a more basic salt and the neutral acetate is formed—

$$2CuO\ Cu(C_2H_3O_2)_2 = Cu(C_2H_3O_2)_2 + Cu(C_2H_3O_2)_2\ 2CuO.$$

Repeated exhaustion with water causes the formation of normal cupric acetate with two other basic acetates thus :

$$5(C_2H_3O_2)_2Cu, CuO = 2(C_2H_3O_2)_2Cu, 2CuO + (C_2H_3O_2)_4Cu_2, CuO + (C_2H_3O_2)_2Cu.$$

The composition of samples examined by Berzelius and Phillips is given in Watts' *Dictionary of Chemistry.*

			Phillips.		
			French.	English	
Theoretical for $(C_2H_3O_2)_2$ CuCuO, $6H_2O$.	Berzelius.			Crystallised.	Compressed.
CuO . . .	43·24	43·34	43·5	43·25	44·25
$(C_2H_3O)_2O$ . .	27·57	27·45	29·3	28·30	29·62
$6H_2O$ . .	29·19	29·21	25·2	28·45	25·51
Impurities .	—	—	2·0	—	0·62
	100·00	100·00	100·0	100·00	100·00

Green verdigris, which according to Berzelius is the salt $2(C_2H_3O_2)_2Cu$, $CuO + 6H_2O$ with small quantities of bi- and tri-basic acetates and sometimes cuprous acetate, is prepared at Grenoble by sprinkling copper plates with vinegar and keeping in a warm damp room, and in Sweden by packing copper plates and flannel alternately and moistening with

vinegar. The greenest kind, Berzelius stated, contains 49·9 per cent. CuO and 13·5 per cent. water and impurities, while the pure sesqui-acetate contains 43·5 per cent. CuO.

Brunswick Green.

The pigment formerly known by this name was oxy-chloride of copper $Cu_4Cl_2O_3$, $4H_2O = CuCl_2\ 3CuO,\ 4H_2O$, prepared by moistening copper turnings with hydrochloric acid or a solution of ammonium chloride and leaving them in contact with the air. The oxy-chloride forms on the surface, and is washed off with water and dried at a gentle heat.

The much used pigment now known by this name is of very different composition, namely, Prussian blue and chrome yellow diluted with barium sulphate.

A preparation of copper oxy-chloride from copper turnings and ammonium chloride gave after drying in the air and then over H_2SO_4—

H_2O lost at 100°	1·4
H_2O lost at 175-85°	15·7
$CuCl_2$	23·0
CuO	60·4
	100·5

It was a blue-green which became greener on drying at 100° and darkened at higher temperatures. It is more basic than required by the formula $Cu_4Cl_2O_3$, $4H_2O$—

$4H_2O$	16·2
$CuCl_2$	30·3
3CuO	53·5
	100·0

Our preparation agrees fairly closely with $2CuCl_2\ 9CuO, 10H_2O$.

It seemed to be a very poor pigment of very little colouring power when ground in oil.

Non-Arsenical Green.

A green brought out in Germany to supersede emerald green consisted mainly of malachite brightened by lead chromate. It is said to be obtained by mixing copper blue (basic carbonate) with chrome yellow, chalk and ferric oxide. We give an analysis by C. Struse:—

Lead chromate	13·65
Malachite	80·24
Ferric oxide	0·77
Calcium carbonate	2·65
Water	2·58
	99·89

It never, we believe, came much into use and in no way equals the brilliance of copper aceto-arsenite.

Copper Blues.

Mountain Blue (*Blue Ashes, Lime Blue, Copper Blue*).—The name mountain blue is given to the mineral azurite, a native carbonate of copper, and also to a blue prepared by precipitating copper hydroxide with lime cream. When cupric sulphate is treated with calcium hydroxide,

$$CuSO_4 + Ca(OH)_2 = Cu(OH)_2 + CaSO_4,$$

the pigment contains copper hydroxide with precipitated calcium sulphate, and when, as is sometimes done, potassium carbonate is mixed with the lime, calcium carbonate also remains in the washed blue. This blue is, we believe, used to some extent for distemper work, but we have never seen a commercial sample.

This substance in the moist condition has, under the name "bouille Bordelaise," been used with success as a spray for checking the ravages of the potato disease, *phytophthyra infestans*. It is a very pure sky-coloured blue.

By precipitating cupric nitrate with chalk and adding

to the precipitate 8 to 10 per cent. freshly burnt lime, a blue of this kind is obtained. Without the lime a green pigment results.

A peculiar blue described by Halich is obtained by dissolving cupric oxide in nitric acid and treating with K_2CO_3 until almost but not quite all the copper is precipitated; then washing the precipitate with water, and introducing it into a solution of copper nitrate. An insoluble heavy green basic nitrate is formed, which, digested with a solution of zinc oxide in potash, forms a dark blue of great body but little weight, which contains both zinc and copper, and is apparently a double oxide with basic copper nitrate.

VIII.—ULTRAMARINE.

Real ultramarine is obtained from a somewhat rare mineral, *lapis lazuli*, a variety of Haüynite thus described by Dana: "Not a homogeneous mineral, according to Fischer and Vogelsang. The latter calls it a mixture of granular calcite, ekebergite, and an isometric ultramarine mineral, generally blue or violet. Much used as an ornamental stone." It is, as the two following analyses will show, of very variable composition:—

Gmelin.		Fuchs.	
Silica	49·0	Phosphoric acid	41·81
Alumina	11·0	Alumina	35·73
Lime	16·0	Magnesia	9·34
Soda and potash	8·0	Silica	2·10
Oxide of iron	4·0	Protoxide of iron	2·64
Magnesia	2·0	Water	6·06
Sulphuric acid	2·0		
	92·0		97·68

These analyses are rather ancient, and though by men eminent in their day, seem very inconclusive. Speaking roughly it would appear to be an aluminium-sodium silicate containing sulphur in some form. It is of a blue colour

varying according to circumstances. Lapis lazuli is the "sapphire" of the ancients and is evidently the material referred to in Revelation xxi. 19. It is occasionally found with gold-like fragments of iron pyrites interspersed through its substance. To prepare the pigment, the mineral is broken into small pieces, freed as much as possible from mechanically adhering impurities, heated in a crucible and thrown into cold water or very weak vinegar. It is then washed by decantation, dried, ground and then purified by elutriation, by which process various grades of colour, from the finest blue to grey ultramarine ash, are obtained. Ultramarine is the purest and most beautiful blue pigment known and most closely approximates in tint to the pure blue of the sky. Real ultramarine, on account of the rarity of lapis lazuli and the troublesome process of preparation, is a most expensive colour.

In the year 1828 Guimet, stimulated by a prize of 6,000 francs offered by the Société d'Encouragement de France, discovered a method of preparing artificially a blue similar in properties and composition to natural ultramarine. Alkali makers had previously noticed spots of ultramarine on their furnaces, and efforts had been made to determine the conditions of formation of this pigment. Gmelin, whose analysis has been quoted, also discovered at about the same time a method of formation.

Blue ultramarine was formerly solely made by the "indirect process," in which sulphate of soda, kaolin and charcoal are ground together and burnt in crucibles in a suitable oven for six to nine hours. The mass is then turned out and is of a dull green colour. It is then crushed and heated on a roasting furnace with powdered sulphur, the mass being continually stirred until the sulphur has burnt off and a bright blue mass is left. Though the materials are cheap the process is troublesome and the result is somewhat uncer-

tain. The product obtained is poor in silica, and though of pure tint is of very weak colour.

The direct process, which is now adopted very largely, requires great care both as to details and in the selection of materials. The mixture consists of about 100 parts of china clay, 90 of soda, 110 of sulphur, 20 of charcoal and a variable amount of infusorial earth, the amount of this latter material depending on the quality of ultramarine required. The china clay must be very pure and free from sand and other rough matters. The soda is the best soda ash, known as carbonated ash, and should test 58 per cent. (total alkali as Na_2O). The raw materials are intimately mixed and finely ground. The ignition is conducted in ovens of either of two patterns, "crucible" or "mass" ovens, of which the latter is the newer, and, in the opinion of some, the better form. The names explain themselves sufficiently; in the former pattern the mixture is filled into crucibles twelve to sixteen inches high, the lids being luted on and rows of these crucibles piled into the furnace, the heat of which is gradually raised to a bright red which is maintained for some hours, the time varying with the size of the crucibles and the nature of the materials used. Air is as far as possible excluded at the close of the operation, and the mass allowed to slowly cool. The crucibles are taken out and opened and the ultramarine carefully turned out and pieces of overburnt material chipped away from the beautiful blue colouring matter. The "mass" ovens are arranged with a permanent floor and back or bridge; the mixture is put on the floor and banked up until level with the bridge, and is then covered with thin tiles luted together with a mixture of sand and clay. A hole is left in front for observing the courses of the operation and another smaller one for removing samples of the burning from time to time. Both these can be closed with loose bricks or clay plugs. The temperature is slowly

raised to a bright red, when sulphurous flames are seen to rise from any cracks or faults in the luting; these at first increase, and as the reaction becomes complete disappear. The temperature is maintained at its highest point for twelve to eighteen hours or until, in the opinion of the operator, all action has ceased. The sample, if properly burnt, is of a greenish blue and evolves sulphur dioxide in the air without actually burning, and spread on a tile soon cools and becomes a slightly greenish blue. The colours assumed by the mixture while burning are successively a yellowish grey (initial) brown, green, blue; the brown colour is unstable and in the air, and the material burns to a greenish blue. The green is also unstable. If the sample is satisfactory the oven is luted up and the mass allowed to cool. This takes a week or ten days; on opening, the mass is a deep blue, the lower portions, having been more or less heated, being less brilliant than the upper layers. The loss in weight is usually about one third, and some considerable shrinkage takes place. The mass is washed with hot water in vats with perforated false bottoms and coarse filter surfaces to remove sodium sulphate and other soluble salts, and is ground between upright stones, settled first to remove dirt and unground matter, and then the finer matter fractionally settled out, the latter portions which settle more slowly being the finer colours. The liquid, which still contains colouring matter, is precipitated with lime, which, by coagulating the particles, renders their removal by filtration more easy. The mixing of the various shades so as to ensure uniformity of product is a matter of considerable importance as, of course, this considerably affects the reputation of the manufacturer.

Most of the details given above are taken from the article by G. W. Rawlings in Thorpe's *Dictionary of Applied Chemistry*.

We give the results of analysis of some samples examined by us and some given in the article mentioned above :—

	German.		English.	German, violet.	Parry and Coste.		
Moisture	—	—	—	—	—	—	0·7
SiO_2 . . .	38·90	39·61	42·70	41·30	42·26	41·7	42·4
Al_2O_3 . . .	29·50	23·95	24·50	24·30	26·79	25·2	24·0
Na_2O . . .	21·02	19·15	19·95	17·40	19·49	18·8	18·7
S . . .	10·84	13·10	13·04	14·80	12·01	14·2	15·4
	100·26	101·66	100·19	101·30	100·55	99·9	101·2

Comparative analyses of three varieties of ultramarine by E. Dollfus and F. Goppelsröder (*Bull. de Mulhouse*, 1875, May; *Dingl. pol. J.*, ccxx., 337, 431) are given below. These are of a more ambitious nature than the others quoted by us :—

	Green.	Blue.	Violet.
Silicon	17·963	19·160	20·440
Aluminium	17·702	13·925	12·735
Sodium as Na_2O . . .	10·487	10·088	11·110
Potassium	0·420	—	—
Sulphur as SO_3 . . .	0·292	0·500	0·877
Sulphur as SO_2 . . .	0·213	0·441	0·834
Sulphur as S_2O_2 . . .	—	0·469	2·536
Sulphur as Na_2S . . .	3·718	3·057	1·165
Free sulphur . . .	3·491	8·977	6·964
Sodium as Na_2 . . .	5·345	4·395	1·676
Oxygen	40·363	38·984	41·748
	99·994	99·996	100·085

These would seem to show that the percentage of silicon increases and that of aluminium decreases from the green to the violet substance. The analyses, calculated as they are to three places of decimals, add up to 100 remarkably closely.

The structure of ultramarine is crystalline, its form being apparently single refracting crystals of the regular system. This fact was first observed by R. Hoffmann, and the above conclusion as to the structure arrived at by H. Vogelsang.

The true constitution of ultramarine is still a matter of great doubt, though its composition and behaviour to reagents have been the subject of investigation on the part of many chemists. It is, to say the least, startling that a compound

containing only the elements silicon, aluminium, sodium, sulphur and oxygen, none of which are recognised as possessing chromophoric properties, should have so intense a colour. The method of production, being of a somewhat violent nature, serves only to a very slight extent to indicate the nature of the pigment. That it is some sort of double silicate containing sulphur is evident; but the internal structure of the blue molecule is, so far, merely a matter for surmise.

The action of reagents tends to throw more light on the probable constitution of this pigment. Mineral acids, both strong and dilute, attack ultramarine blue, discharging the colour and causing an evolution of hydrogen sulphide with liberation of sulphur. This seems to point to the existence of a polysulphide. Solutions of alkalies do not attack blue or green ultramarine but the violet becomes blue. A solution of alum slowly decolourises blue ultramarine. Heumann discovered this; when blue ultramarine is heated to 120°C. in a sealed tube with a solution of silver nitrate for fifteen hours a dark yellow amorphous body having the following composition is formed:—

Ag	47·97
Na	1·07
Al	9·1
Si	10·09
S	4·75
O and H (? H_2O)	0·61
Insoluble siliceous matter (clay)	0·81
	74·40

It is to be presumed that the difference between 74·4 and 100·0 is oxygen, which is not mentioned in this analysis.

It will be seen that in this compound nearly all the sodium has been replaced by silver; it is probable that all is replaceable. This compound, silver ultramarine, forms the starting point for organic derivatives as ethyl, benzoyl and amyl ultramarines; the existence of these substances, though of

interest, can scarcely be said to throw much light on the constitution of the parent substance. In addition to these organic ultramarines, potassium (blue), lithium (blue), barium (yellowish-brown), zinc (violet) and manganese (grey) ultramarines may be formed. In all these cases the silver compound is acted upon with the iodide or chloride of the radical or metal to be substituted. The sulphur of ultramarine may be replaced by selenium or tellurium.

When a mixture of chlorine and steam is passed over ultramarine blue or green heated to 160° to 180° a violet-coloured substance from which sodium chloride may be extracted is produced. The same substance is produced by the action of hydrochloric acid gas and air at 150° to 230° C. This substance, ultramarine violet, contains the whole of the sulphur of the original blue, but the sodium (partly removed as chloride) is considerably reduced in amount. The long-continued action of hydrochloric acid and air causes the violet substance to become rose red, or the red colour may be prepared by passing the vapours of nitric acid over the violet at 130° to 150° or by the vapours of hydrochloric acid at 128° to 132°.

The considerable variation in composition of ultramarines of similar colour, and on the other hand the similarity in composition of pigments of differing shades, seem to point to the conclusion that ultramarine is not a simple substance, either being a mixture of blues of allied composition or of a coloured with a colourless substance.

Notwithstanding the difficulties of the case various workers have from time to time proposed formulæ for expressing the constitution, or, at any rate, the empirical formulæ of ultramarine substances.

R. Hoffmann (*Ann.*, cxciv., 1-22) considers that the pale blue kind, poor in silica, has the formula $4(Na_2Al_2Si_2O_8) + Na_2S_4$, and that rich in silica and of a deep reddish tint is $2(Na_2Al_2Si_3O_{10}) + Na_2S_4$. These, he supposed, are formed

by the abstraction of sodium from a white compound, thus :—

	White.		Blue.
Blue, poor in silica	$4(Na_2Al_2Si_2O_8 + Na_2S) - 6\,Na$	$=$	$4(Na_2Al_2Si_2O_8) + Na_2S_4$,
Blue, rich in silica	$2(Na_2Al_2Si_3O_{10} + 2\,Na_2S) - 6\,Na$	$=$	$2(Na_2Al_2Si_3O_{10}) + Na_2S_4$,

the effect of this being to form polysulphides to which the colour is probably in some way attributable. The latter white ultramarine has not been discovered.

Grünzweig found that yellow ultramarine, rich in silica, could be made from the blue to which the formula $2(Na_2Al_2Si_3O_{10} + Na_2S)$ is attributed, by the abstraction of sulphur and the addition of oxygen, thus $2(Na_2Al_2Si_3O_{10}) + Na_2S_3O_4$ is formed, the yellow thus appears to be an oxidation product of the blue.

Ungor considered that ultramarine contained nitrogen and was $Al_2SiO_2O_3N_2$.

Endemann believes in the existence of a "colour nucleus," which in the case of white ultramarine is $AlNa_4O_2S_2$.

Böttinger (*Ann.*, clxxxii., 305) holds that ultramarine may be regarded as the last term of a series of molecular compounds of an aluminium silicate with a sodium thio-silicate—a silicate in which more or less oxygen is replaced by sulphur.

Fürstenau (*Dingl. pol. J.*, ccxix., 269) finds that only the silicates $4Al_2O_3$, $9SiO_2$ and Al_2O_3, $3SiO_2$ are suitable; these treated with Na_2S_2 or Na_2S_5 give the following pigments :—

(*a*) $4Al_2O_3$, $9SiO_2$ with Na_2S_2, pure clear blue of but little colouring power.
(*b*) $4Al_2O_3$, $9SiO_2$,, Na_2S_5, pure dark blue with great covering power.
(*c*) Al_2O_3, $3SiO_2$,, Na_2S_2, reddish, dingy-coloured product.
(*d*) Al_2O_3, $3SiO_2$,, Na_2S_5, dark violet blue colour with great tinctorial power.

The former two products are free from alum, but the latter two both contain this substance.

Considering the difficulties attending all investigations into the constitution of inorganic compounds, it is not surpris-

ing that diversity of opinion should exist as to the true nature of ultramarine; we have endeavoured to indicate the views of some workers on the subject, but cannot profess to have any preference for the views of any one individual. There is certainly an abundant field for work in this direction.

The method of analysis adopted by us was to treat a portion of about 1 gram in a platinum or porcelain dish with hydrochloric acid, carefully covering and, when effervescence had ceased, washing back any splashes into the main liquid. This was evaporated to dryness in the water bath, moistened with hydrochloric acid and again taken to dryness. The dry mass was moistened with hydrochloric acid, taken up with water and the soluble part filtered from the residue of insoluble matter and sulphur. This insoluble matter was ignited and weighed, afterwards being examined to ascertain whether pure silica or not. The alumina is precipitated by addition of a slight excess of ammonia, collected, and weighed in the usual way. The ignited alumina should be quite white, any colour indicating the presence of impurity. The filtrate from the alumina contains the alkali (as chloride). This may be determined, after addition of sulphuric acid in excess and evaporation to dryness in a platinum vessel, by cautiously igniting at a very low temperature just sufficient to drive off the ammonium salts and sulphuric acid; the sodium is thus obtained as neutral sulphate Na_2SO_4. It is better to weigh as sulphate than as chloride, as the latter is volatile at a relatively low temperature and loss is likely to occur.

For the determination of sulphur it is sufficient to evaporate to dryness with concentrated fuming nitric acid or aqua regia, which oxidises sulphur to sulphuric acid. This can be determined in the filtered diluted liquid in the usual manner.

Various methods of examination as to quality have been described by different workers. Some of the more reasonable of these are described below.

Guimet, the discoverer of artificial ultramarine, compared blues as to colouring power by weighing out 0·1 gram of a standard sample and mixing it with 0·6 gram of pure powdered chalk by means of a thin spatula, and diluting a similar quantity of the sample to be examined with weighed increments of the same chalk until equal tints were obtained. Then if the sample under examination requires ·7 gram (7 times its own weight) to produce the standard tint, the colour value standard : sample = 6 : 7, that is, the sample is $\frac{1}{6}$ better than the standard.

Another rather remarkable method of examination is to ignite at a temperature of about 400° C. in a current of hydrogen. The best samples of the artificial blue become a greyish green in about half an hour, the worst in a few minutes. Lapis lazuli heated for as long as two hours retains its colour in the presence of hydrogen.

Büchner adopts an alum test; 0·05 gram ultramarine is stirred up with a cold saturated solution of alum and the time required for decolorisation, whether minutes, hours or days, noted. The longer the blue resists the action of alum the better it is likely to be.

The fineness of grinding and the glazing power of the blue put on paper with size are matters of importance more particularly to the paper maker.

IX.—CARBON PIGMENTS.

Carbon forms the base of most of the black pigments used in the arts. In most of these it is employed in some amorphous form, but for the protection of metal-work and as a grey paint the mineral graphite finely powdered is used, ground in oil. Graphite (plumbago, black lead) is almost pure carbon; its value as a protective coating for iron-work has been considered in chapter ii. (p. 47). It has the advantage of

being an absolutely inert substance and can only act as a body or rather, perhaps, a skeleton for the boiled oil varnish which forms when the paint dries. When the paint becomes waterlogged the fact of graphite being strongly electro-negative to iron is hardly in its favour.

The various carbon paints have no great "drying" properties in oil, and require the use of "boiled" oil or of suitable siccative materials.

Ivory Black (*Bone Black*).—By the ignition of ivory (waste pieces, turning dust, etc.) or bone in a covered vessel a good black pigment is obtained. The organic matter (ossein and traces of fat) is charred to carbon, and a mixture of this with phosphate and carbonate of lime left behind as either ivory or bone black. The former, though much of the black sold for ordinary purposes is called ivory black, is probably only used by artists' colourmen, if, indeed, by them, and the cheaper bone black sold for decorators' work.

We give the composition of average bones and of samples of so-called ivory black:—

	Bones.	Ivory Black.		
Moisture	6·91	3·44	1·2 Oil	28·84
Organic matter (or carbon)	39·31	20·03	13·0	12·82
Phosphate of lime	46·60	73·47	84·8	49·10
Carbonate of lime, etc.	5·78			3·24
Sand	1·40	3·06	1·0	6·00
	100·00	100·00	100·0	100·00
Nitrogen	4·35			

Ivory black is sometimes moulded into little conical masses—probably a little gum is used to give some coherence—and sold as soap black; we give the composition of a sample examined by us:—

Moisture	3·29
Loss on ignition (black)	23·41
Phosphate of lime, etc.	70·71
Insoluble siliceous matter	2·59
	100·00

The peculiar manner in which the inorganic matter is incorporated with the black in this dye, though diminishing its pigmentary power, gives it a beautiful softness in working which renders it a valuable colour.

Lamp Black (*Soot Black*, *Vegetable Black*).—When organic matters rich in carbon are burnt a great deal of unburnt carbon escapes as "smoke" and condenses, or rather settles

Fig. 5.

out as "soot" on the cooler parts of the chimney or other draught arrangement. To obtain such black in quantity resin or tallow is burnt in a confined atmosphere and the carbon liberated collected on the walls of a large chamber, which are hung with canvas; a cone suspended in this chamber, on lowering, acts as a scraper and detaches the black which falls on to the floor. The accompanying illustration represents

the manufacture of this pigment, the resin or tallow is burnt in the iron pot A, heated by the furnace B. The soot is condensed in C and scraped off by the cone D.

Bistre.

This is a brownish-black pigment produced by extracting with boiling water soot produced at a very low temperature, and consequently containing a considerable amount of empyreumatic matter. The residue, when this has been extracted, is levigated and dried. It forms a warm brownish black. It is said to be principally produced from beechwood smoke or soot.

X.—VARIOUS UNCLASSIFIED PIGMENTS

(*Naples Yellow*).

Under the name of Naples yellow various pale yellow pigments are sold. The original Naples yellow (giallolini) appears to have been the secret preparation of a Neapolitan colour maker. Fongeroux de Bonduroy, who made some investigations at Naples, where it was by some believed to be obtained from some volcanic product from the adjacent mountain Vesuvius, gives the following method of preparation: A mixture of 24 parts of white lead, 4 parts of "diaphoretic antimony" (potassium metantimoniate), 1 part of ammonium chloride and 1 part of alum are fused in an earthen crucible at a red heat for three hours and the melt broken up on cooling, ground and washed.

Thénard states that this pigment is said to be obtained by the "calcination at the proper temperature of a mixture of litharge, hydrochlorate of ammonia (sal ammoniac), diaphoretic antimony (a combination of peroxide of antimony and potassa and alum)". Another method is to fuse 3 parts of massicot (litharge) with 1 of antimony oxide, or to fuse 2

parts of red lead, 1 of antimony and 1 of calamine (zinc carbonate).

Brunner recommends slow fusion of 1 part of tartar emetic with two parts of lead nitrate and washing the ground melt with hydrochloric acid to brighten its colour.

From these processes, which are evidently variations of one original method, it would appear that the pigment is a more or less basic antimoniate of lead with various impurities added according to taste.

In his Cantor Lectures (1891) Mr. A. P. Laurie describes various pigments which have been included under the name of Naples yellow. We quote the section on this pigment, of lecture ii. :—

"*Giallolino.*—The history and nature of this pigment are somewhat obscure. Cennino distinctly states that it is a volcanic product. He states that it is not a brilliant yellow, though brighter than ochre, and never makes bright greens. Mrs. Merrifield considers that several pigments were included under this name. I cannot do better than quote her summing up of this matter.

"1. 'A native mineral yellow pigment, known by the name of *giallolino, giallolino di Napoli, jaune de Naples, luteolum Napolitanum.*'

"This is doubtless the yellow referred to by Cennino. All trace of it seems to be lost, though probably a proper search in a volcanic district would lead to its discovery.

"2. 'An artificial pigment which was composed of the yellow protoxide of lead, and which was called *giallolino, giallolino fino, giallolino di fornace di fiandra, luteolum Belgicum genuli* (the last is a Spanish term) and *massicot,* of which there are two varieties, namely, the golden or yellow, and the white or pale *massicot.*'

"This pigment can be prepared by gently roasting white lead. It is now known as Turner's yellow. It is apt to turn

black, like all lead pigments, the fault of our towns, not of themselves.

"3. 'An artificial pigment made at Venice, composed of *giallolino fino* and a certain kind of *giallo di vetro*, or vitreous yellow, for which a recipe is given in the Bolognese MS. in the Venetian dialect, and which appears to have been the Hornaza of the Spaniards.'

"This recipe is worth quoting, and is as follows:—

"'To make yellow glass for paternosters or beads: Take of lead 1 lb., of tin 2 lb.; melt and calcine them, and make glass for paternosters.

"'To make giallolino for painting: Take 2 lb. of this calcined lead and tin, that is, 2 lb. of this glass for paternosters, 2½ lb. of minium, and ½ lb. of sand pounded very fine; put it into a furnace and let it fine itself, and the colour will be perfect.'[1]

"This pigment must have been a yellow lead frit. Probably effective on fresco walls, but of little or no use in oil. Mrs. Merrifield then goes on:—

"'I consider it established that they used two kinds of Naples yellow, namely:—

"'1. A native mineral pigment found in the neighbourhood of volcanoes, the nature of which is not accurately known, and which was called "giallolino di Napoli" and "jaune de Naples," and which is synonymous with the first kind of giallolino above mentioned.

"'2. An artificial pigment now in use (?) composed of the oxides of lead and antimony, called "giallo di Napoli," "jaune de Naples," and Naples yellow, and which was not known to the old Italian artists.'

"Apparently the manufacture of the more modern artificial Naples yellow has now ceased. I failed to find either that

[1] "MS. of the fifteenth century in the library of the R. R. Canonica Regolari, in the Convent of the S. Salvatore in Bologna."

it was made or that any one had ever heard of its being made in Naples. The manufacture has long ceased, apparently. The colour now sold as Naples yellow is, I understand, usually a mixture of yellows. One sample I examined was massicot pure and simple. A fine yellow can be made from lead and antimony, and I have some here which I have made myself. Possibly a search on Mount Vesuvius might result in the rediscovery of the original Naples yellow."

Arsenic Sulphides (*Orpiment, Realgar*).

Of the three sulphides of arsenic As_2S_2, As_2S_3 and As_2S_5 the first two are used as pigments, to some extent. They may both be formed artificially, or suitable specimens of the native mineral may be ground.

Realgar, *Arsenic disulphide.*—This occurs native as an aurora red or orange yellow mineral of the monoclinic system, of resinous lustre, transparent to translucent, of uneven conchoidal fracture. Specific gravity 3·4 to 3·6. It may be obtained artificially by fusing 75 parts of arsenic with 32 parts of sulphur (it is probably better to use the proportions 2 : 1 as loss of sulphur is likely to occur on fusion). It is distillable in a confined atmosphere but on heating in the air burns to As_2O_3 and SO_2.

Orpiment (*Auri pigmentum, King's yellow, Royal yellow*). *Arsenic trisulphide.*—Orpiment occurs in nature as a lemon-yellow substance found in foliated masses varying considerably in shade. Its specific gravity is about 3·4 to 3·5. It belongs to the orthorhombic system.

It is usually prepared in the wet way by precipitating solutions of arsenious acid containing free hydrochloric acid with hydrogen sulphide—

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O.$$

It can also be prepared by fusing arsenic or arsenious

acid with the proper proportion of sulphur. In the former case direct combination occurs, in the latter sulphur dioxide is formed.

$$2As_2O_3 + 9S = 2As_2S_3 + 3SO_2.$$

The sulphide sublimes to the cooler parts of the vessel.

Orpiment appears to be fairly permanent in oil though liable to be blackened when used in *tempera*. Both orpiment and realgar, being sulphides, must be used with very great caution in admixture with other pigments. Mercury, lead and copper pigments should not be used in admixture with these colours.

Cadmium Yellow, Radiant Yellow, Cadmium Sulphide CdS.

Cadmium sulphide, which is a brilliant yellow substance, is used to a considerable extent as a pigment. It is usually prepared by the precipitation of a solution of a cadmium salt with hydrogen sulphide. In the case of the sulphate

$$CdSO_4 + H_2S = CdS + H_2SO_4.$$

The bright yellow precipitate is collected, washed and ground. It is not entirely permanent, as will be seen on reference to Russell and Abney's experiments already quoted.

Cadmium yellow is also prepared by fusion of cadmium oxide with sulphur.

Vandyck Brown.

Vandyck brown is a name applied to various brown pigments owing their tints to either ferric oxide or organic matter (sometimes partially charred) or both. Church describes three varieties: "The first is made by calcining certain very ferruginous earths or brown ochres; the second is nothing more than a dark brown variety of colcothar; the third is a kind of brown earth, containing, along with some iron oxide and hydrate, a good deal of organic substance in the form of humus, or bituminous matter. The

first and second kinds are permanent and innocuous, but the third kind will not resist the prolonged action of light, becoming paler and redder in course of time."

Prof. Church further states that most of the samples now met with in England belong to the third kind.

We have examined some used for decorative purposes and found them to belong to the third class. The figures are given below.

	Dry Brown.	Brown in Water.		Brown in Oil.
Moisture . . .	12·25	60·6	50·35	—
Mineral matter . .	6·55	7·6	9·50[1]	—
Organic matter . .	81·20	31·8	40·15	62·56
Oil	—	—	—	28·85
Oxide of iron and alumina	—	—	—	1·81
Carbonate of lime, etc. .	—	—	—	5·16
Insoluble in HCl . .	—	—	—	1·62
	100·00	100·0	100·00	100·00

Two samples of artists' colours were examined with the following results:—

Oil	40·9	82·5
Organic matter	38·5	
Oxide of iron	4·4	10·7
Alumina	4·6	
Lime salts, etc.	5·4	3·9
Insoluble in acid	6·2	2·9
	100·0	100·0

These are both rather organic than oxide of iron pigments and their permanence may well be a matter for doubt.

[1] Including

Oxide of iron and alumina	3·00
Carbonate of lime	4·05
Insoluble siliceous matter	2·45
	9·50

CHAPTER IV.

ORGANIC PIGMENTS.

I.—PRUSSIAN BLUE.

THE pigment generally known as Prussian blue is a mixture of double cyanides of iron, although a definite single compound is known which has a claim to the name. In the process of manufacture on a commercial scale, however, it is impossible to prepare this pure compound, so that the pigment is invariably a mixture. In this sense, then, Prussian blue will be referred to in the sequel. Alone, or diluted with an inert white base, it forms a very valuable paint, known under the names Prussian blue, Paris blue, Antwerp blue, or Chinese blue. When genuine it should not be diluted, and under the above names one expects to receive the pure blue. Several fancy names have been introduced for the diluted pigment, and in estimating the value of these compounds it is hardly necessary to say that their value is directly proportional to the amount of the true pigment they contain. Prussian blue also forms the base, together with lead chromate, of the well-known Brunswick green paint.

History.—The historical aspect of this important pigment is of some interest on account of the fact that that of the cyanogen compounds as a group may be said to have commenced with the manufacture of Prussian blue. This was accidentally discovered in the early part of the eighteenth

century by a colour manufacturer of the name of Diesbach. He shortly afterwards communicated the fact to the chemist Dippel, who was an alchemist, and he carefully investigated the conditions under which the colouring matter was formed. Woodward first, however, published a method of making it. He stated that it was obtained by heating equal parts of cream of tartar and nitre, and heating strongly the resulting alkaline mass with ox blood. The residue of the calcination was then lixiviated, and green vitriol (sulphate of iron) added, together with alum. A greenish precipitate was thrown down, which on treatment with hydrochloric acid yielded the blue colour (*Phil. Trans.*, 1724). Various other animal matter was soon shown to yield the same result. It is unnecessary here to go into the various views which were in the early days held as to the constitution of the pigment, all of which were later proved to be erroneous. Macquer in 1752 showed that the use of alum was not necessary. The first real indication of its constitution was given by the last-named chemist, who showed that when boiled with alkali it yielded oxide of iron, leaving a new body in solution. To this substance, which we now know as potassium ferrocyanide, the name phlogistigated potash was given. Towards the end of the eighteenth century Scheele investigated the compound, and the result was the discovery of that deadly poison, prussic acid. A few years later Berthollet took up the investigation, and to him and Guy-Lussac we owe our first real insight into the molecular constitution of the double cyanides.

Before passing on to the study of the actual constituents of the commercial pigment, we may briefly examine the principles underlying the process of its manufacture. The production of the pigment is intimately connected with the manufacture of the well-known salt prussiate of potash (the yellow prussiate, potassium ferrocyanide), so that it is necessary to describe the manufacture of the latter. Animal matter,

such as the shavings of hoofs, horn, dried blood, skin or hair, is used as the source of the carbon and nitrogen in the compounds. Owing to the large quantity of nitrogen these substances contain, they were sometimes calcined alone in the first instance in order to obtain as much ammonia as possible. Sufficient nitrogen, however, is retained for the production of the cyanogen required for the prussiate. The charred organic mass is mixed with potassium carbonate (this is preferably added in strong solution, and the water afterwards driven off). The mixture is then heated in a cast-iron retort, the iron necessary being taken up from this, or, as preferred by some manufacturers, scrap iron is added to the mass. The mass is then extracted with water and the water filtered off and boiled down. A series of recrystallisations is necessary to obtain the prussiate in a state of purity, and excess of carbonate of potassium should be avoided. For the manufacture of ordinary Prussian blue, however, the crude solution is frequently employed, and it is only in the finer varieties that the pure crystals are first separated. Processes have been patented for the recovery of ferrocyanides from gas and soda liquors, and at least one of the large gas companies is now employed in the manufacture of Prussian blue. The blue pigment is obtained in many different shades, and the methods used are as variable in detail as is the composition of the resulting pigment. In general the principle of the process is the addition of either a ferric salt to the solution of the prussiate, or of a ferrous salt, the resulting nearly colourless precipitate being treated with a suitable oxidising reagent such as nitric acid, ferric chloride, or bleaching powder. According to A. H. Allen the lighter shades are useful for the manufacture of zinc greens and the darker for the preparation of chrome greens. Gentele states that the best blues are obtained by using a ferrous salt and oxidising the ferrous ferrocyanide formed. In the process recommended

by Crowther and Rossiter the ferrous ferrocyanide is suspended in strongly acidulated water, and submitted to electrolysis. A blue of extremely vivid violet reflex is obtained at the anode.

Various allied compounds of iron and cyanogen, with or without potassium, are well known. These result from the treatment of ferrocyanide or ferricyanide with ferrous or ferric salts. In theory, one definite compound may be stated to result in a given reaction, but owing to the oxidation by the atmosphere, to impurities in the salts, and to other uncontrollable circumstances, a mixture always results in practice. The following table gives the well-defined members of this series :—

Compound.	Formula.	Common Name.	Reaction between
1. Potassio-ferrous-ferro-cyanide	$K_2Fe_2C_6N_6$	Everitt's salt	Ferrous salts and ferrocyanide
2. Potassio-ferric-ferro-cyanide	$KFe_2C_6N_6$	Williamson's blue	Ferric salts and ferrocyanide
3. Dipotassio-diferric-diferrocyanide	$K_2Fe_4C_{12}N_{12}$	Soluble Prussian blue	Ferric salts and ferrocyanide
4. Ferric ferrocyanide	$Fe_7C_{18}N_{18}$	Prussian blue	Ferric salts and ferrocyanide
5. Potassio-ferrous-ferri-cyanide	$KFe_2C_6N_6$	Williamson's blue	Ferrous salts and ferricyanides
6. Ferrous ferricyanide	$Fe_5C_{12}N_{12}$	Turnbull's blue	Ferrous salts and ferricyanides

Which of these bodies, 2 or 5, actually represents Williamson's blue is not certain, but the two bodies are practically, if not actually, identical.

For all practical purposes the blue sold on the market under the name of Prussian blue may be regarded as a mixture of iron and iron-potassium ferrocyanides.

The Analysis of Prussian Blue.—Full details as to the methods of analysis of this important pigment were described by us in a paper published in the *Analyst* (September, 1896), from which we quote the following description in full :—

"We have found, and Dr. Williamson in every case found, that alkali was present in so-called Prussian blue, not merely as alkaline salts not washed away completely, but as an integral part of the cyanide.

"As we are frequently called upon to examine commercial samples of Prussian blue, and of pigments containing this substance, we have considered it desirable to make a more complete examination than the method usually adopted would afford of specimens of blue of known origin, with a view to getting some more definite data for basing conclusions as to the purity of samples of unknown make.

"It appeared to us that, more especially in the case of complex pigments ground in oil, the determination of the nitrogen would give valuable information as to the amount of Prussian blue present.

"Dyer has shown (*Chem. Soc. Journ.*, 1896, 811) that ferrocyanides and ferricyanides yield the whole of their nitrogen as ammonia when treated by the Kjeldahl-Gunning-Arnold method. We found that potassium ferrocyanide boiled with sulphuric acid for a few minutes gave up all its nitrogen as ammonia. A determination of the water of hydration (lost at 180° to 200° C.) was also made. The results were:—

	Found.	Theory.
N	19·64	19·95
H_2O	12·79	12·71

"We therefore felt justified in assuming that equally correct results would be obtained in the case of the allied compounds contained in commercial Prussian blue, an expectation which was fully justified by the agreement of the nitrogen determinations with the other figures obtained.

"The following is briefly the scheme of analysis adopted by us:—

"The moisture is determined at 100°. The water of combination—if the term is here justifiable—can scarcely be determined unless the blue is 'burned' and the water col-

lected, as we made several attempts to drive off the water in a current of hot air, gradually raising the temperature until at 230° C., when water appeared to be still coming off, the pigment was decomposed with the formation of ferric oxide. Dr. Williamson, in his classical paper, 'On the Blue Compounds of Cyanogen and Iron,' determined the total water in these pigments by combustion with plumbic chromate. This is apparently the only way of obtaining a correct result, as, on heating, part of the hydrogen is evolved as hydrocyanic acid, the oxygen of the water going to form ferric oxide, as stated. The nitrogen was determined as above described, and was found to differ within small limits. A weighed quantity was ignited, care being taken that the temperature was sufficiently high to decompose the last traces of the blue, but not too high to render the oxide of iron difficult of solution. It is necessary to ensure the complete oxidation of the finely divided iron, as otherwise it is very difficultly soluble in hydrochloric acid.

"In all cases on adding acid to the 'ash,' a marked effervescence showed that alkaline carbonate (from the alkali-containing ferrocyanide) was present. Pure blue leaves an 'ash' completely soluble in hydrochloric acid, but in the case of adulterated Prussian blue or of diluted blues, barium sulphate or other insoluble matter must be filtered off and weighed before precipitating with ammonia. The iron in the (weighed) mixed oxides was determined by titration with potassium bichromate after reduction with stannous chloride, the alumina being of course estimated by difference. A portion of the filtrate was evaporated to dryness, and, after volatilisation of the ammonium salts, the alkaline salts were weighed, and the chlorine therein determined by titration with silver nitrate. In another portion of the filtrate the sulphuric acid was determined, and from these data—*viz.*, the weight of the alkaline salts, chlorine and sulphuric acid—we were

enabled to show that in all cases the alkali-metal was almost entirely potassium or sodium, and in no case a mixture of the two metals. Another weighed quantity of the pigment was boiled for a few minutes with aqueous potash, and the resulting precipitate of oxide of iron weighed, after ensuring its complete conversion into Fe_2O_3. This, multiplied by 0·7, represents the 'extra-radicle' iron.

"The following tables represent the composition of eight samples of blue sold by makers of repute as genuine Prussian blue of good quality :—

COMPOSITION OF EIGHT SAMPLES OF COMMERCIAL 'PURE' PRUSSIAN BLUE.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Moisture (lost at 100° C.)	5·61	3·54	5·36	5·45	74·53	5·32	5·56	5·61
Water of combination, etc.	15·46	18·18	6·22	13·07	3·08	7·86	14·60	16·93
Cyanogen [1]	37·72	41·10	42·97	37·90	10·64	39·91	40·19	40·86
Iron [2]	29·48	32·16	34·27	30·32	7·97	30·94	31·94	31·25
Aluminium	1·82	·52	—	3·17	·72	1·00	1·43	1·52
Alkali metal (Na)	7·60	(K) 4·50	(K) 7·72	(K) 2·25	(K) 1·06	(K) 11·31	(Na) 2·52	·76
Alkaline sulphate	2·31	—	3·46	7·84	2·00	3·66	3·76	(Na) 3·07
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
[1] Nitrogen	20·31	22·13	23·14	20·18	5·73	21·49	21·64	22·00
[2] 'Extra-radicle' iron	16·66	18·99	19·05	16·04	—	16·21	18·98	19·38

COMPOSITION OF DRY MATTER OF ABOVE SAMPLES (DRIED AT 100° C.).

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Water of combination, etc.	16·38	18·85	6·58	13·87	12·03	8·35	15·46	17·95
Cyanogen [1]	39·96	42·61	45·41	40·06	41·77	42·14	42·55	43·29
Iron [2]	31·23	33·34	36·21	32·05	31·30	32·67	33·82	33·09
Aluminium	1·93	·54	—	3·35	2·90	1·03	1·52	1·61
Alkali metal	8·05	4·66	8·16	2·38	4·16	11·94	2·67	0·81
Alkaline sulphate	2·45	—	3·64	8·29	7·84	3·87	3·98	3·25
	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00
[1] Nitrogen	21·52	22·94	24·45	21·57	22·49	22·69	22·91	23·30
[2] 'Extra-radicle' iron	17·65	19·69	20·02	16·95	—	17·12	20·09	20·51
Intra-radicle iron (found)	13·58	13·65	16·19	15·10	—	15·55	13·73	12·78
Intra-radicle iron (calculated from nitrogen)	14·34	15·30	16·30	14·38	14·99	15·12	15·28	15·54

"In looking at these figures, it will be seen that the percentages of iron and nitrogen do not vary greatly. The amounts of iron in the iron-cyanogen radicle, calculated from the percentage of nitrogen and from the difference between total and extra-radicle iron, do not agree closely in all cases. We can offer no explanation of this. Taking the figures for the dry matter, the greatest difference in iron was in the cases of III. and I., 4·98 per cent., and the greatest difference in nitrogen—between III. and I. again—2·93—differences which, calculated on the mean percentages, are under 16 and under 13 per cent. of the totals respectively.

"It will also be noticed that seven out of the eight samples contained aluminium. This is not to be considered as an adulterant, as alum is often added to the sulphate of iron used in precipitating the ferrocyanide without any idea of adulteration, but probably to cause the precipitate to settle better and to dry in a more coherent manner. It probably exists as aluminium ferrocyanide, a compound described by Tissier (*Comp. rend.*, xlv., 232). This has no colouring properties, and, of course, the iron and nitrogen in the iron cyanogen radicle of this compound appear in the total iron and nitrogen as determined. If merely the *ammonia precipitate* is taken and called 'ferric oxide,' the alumina is included as oxide of iron.

"We think that the addition of alum to the precipitating tank is unnecessary, especially as the best sample of blue we have examined contained none.

"Alkali metal, as iron-akali cyanide, is present in every case. This agrees with the statement of Williamson and others that a blue cannot be obtained free from alkali metal, except when hydroferrocyanic acid is substituted for alkaline ferrocyanide in the manufacture (the alkaline sulphate present in each case is, of course, due to imperfect washing).

"In fact, Prussian blue, if by that term we mean ferric

ferrocyanide $Fe_7(CN)_{18}$, is not known to the commercial world. Commercial Prussian blue is a mixture of Williamson's blue with other iron-alkali cyanides, and often with aluminium-iron cyanides, altogether a most complex substance.

"An examination of the watery extract showed, in the cases of I. and VI., the presence of alkaline ferrocyanide. This is rather remarkable, as with the quantities usually taken the iron is in excess. We believe that these came from the same maker, but are sure, however, that both samples were sent out as *bonâ-fide* Prussian blue.

"The following notes on appearance of the samples in lump and in powder, depth of colour, etc., may be of interest:—

Condition.	Appearance.	Powdered Samples.	
		Classification in order of Depth of Colour.	Quality of Tint.
I. Lumps, conchoidal fracture	Blackish copper glance, but not a bright sheen	2	6
II. Lumps	Blue, pale-looking, no coppery glance	6	4
III. Lumps, conchoidal fracture	Rich blue, bright coppery sheen	4	1
IV. Lumps, conchoidal fracture	Ditto, but not as good as III.	3	2
V. Paste	Dried, with coppery lustre	—	—
VI. Lumps, conchoidal fracture	Blackish coppery glance, but not a bright sheen	1	7
VII. Powder	—	7	5
VIII. Lumps	Light blue, no coppery glance	5	3

"The mean percentage of iron in the dry matter of these eight samples was 32·96. This would give 3·03 as the factor for calculating iron to Prussian blue. The mean percentage of nitrogen was 22·73; this would give as a factor for calculating nitrogen to Prussian blue 4·4. The following tables show the accuracy to which these factors gave the percentage of Prussian blue in the eight samples examined:—

In Dry Matter.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
N × 4·4	94·69	100·98*	107·58	94·91	98·95	99·83	100·80	102·52
Fe × 3·03	94·63	101·02	109·71	97·11	94·84	93·99	102·47	100·26

"Of course, these are merely empirical factors, based on the examination of commercial samples of varying composition, and do not possess the accuracy of a factor to reduce one definite chemical compound to terms of another, but, at any rate, taken together they are of sufficient accuracy for calculating the percentage of Prussian blue in pigments containing that colour. The nitrogen alone in most cases would be sufficient.

"We feel justified in stating that blue sold as Prussian blue should contain at least 20 per cent. of nitrogen and 30 per cent. of iron calculated on the dry matter, and, after burning, should be entirely dissolved by hydrochloric acid. A 'dry' blue should certainly contain under 7 per cent. moisture. Another important point is that the sulphuric acid used in the Kjeldahl nitrogen determination should not be blackened. Pure cyanides dissolve in sulphuric acid without any charring, which, if it occurs, indicates the presence of organic adulterants. A case of this kind will be noted later.

"The watery extract should not indicate the presence of excess of alkaline ferrocyanide. We consider that this is evidence of defective manufacture, although it cannot, of course, be regarded as adulteration. Still it—containing as it does iron and nitrogen—is partly included in the analysis as Prussian blue, whereas it has no pigmentary value, and its solubility in water does not add to the weathering qualities of the colour.

"COMMERCIAL PIGMENTS.

"The following cases of examination of an adulterated sample of Prussian blue (of German manufacture) and of some colours ground in oil possess some interest.

"A rather pale-looking sample of dry powdered Prussian blue, which we were told was a cheap sample of German manufacture, gave only 14·35 per cent. of nitrogen. This at once aroused our suspicions, especially as, instead of becoming colourless in a few minutes on boiling with sulphuric acid, a decided blackening occurred. This clearly pointed to the presence of an organic adulterant. On further examination, the following figures were obtained:—

Moisture	11·35
Water of combination, organic adulterant, alkalies, etc.	37·76
Cyanogen[1]	26·65
Iron	22·67
Aluminium	1·14
Insoluble	·43
	100·00
Per cent. nitrogen × 4·4	63·10
„ iron × 3·03	68·69

This sample not only contained more water than is usual, but was clearly deficient in blue. We think that one is justified in stating that it did not contain more than 70 per cent. of Prussian blue.

"Two samples of 'celestial blue' gave the following results:—

	Dry.	Ground in Oil.
Prussian blue	7·12	6·29
Barium sulphate	92·88	75·60
Oil	—	13·94
Undetermined	—	4·14

"In the case of colours ground in oil, the Kjeldahl method is particularly applicable for the determination of nitrogen,

[1] Nitrogen . . . . . 14·35

and, as now it is very general to sell these colours in oil instead of dry, we think that the nitrogen determination will be found a very convenient method of ascertaining (approximately) the amount of Prussian blue in the many diluted colours made from it. Adulteration with nitrogenous matter is not probable, and so is not likely to lead to erroneous results. We intend to continue the examination of all samples which come under our notice by this method, which is rapid (we have obtained a result in under one hour), and at once points to any serious sophistication."

Prussian blue occurs in commerce as amorphous lumps with a conchoidal fracture, and a strong coppery lustre, which varies much in different samples, the best samples showing a very strong lustre. It is so dark in this state that its real colour value cannot be judged whilst the pigment is in an undiluted condition. The actual value in this respect can best be judged by comparing a carefully ground mixture of 5 per cent. of a standard pure blue and 95 per cent. of white lead with a similarly prepared mixture of the given sample. More of the sample is added if necessary to equalise the two shades, when the colour values are in the inverse ratio to the amount of blue present in the mixtures.

Commercial samples, especially cheap German blues, are often adulterated with barium sulphate, gypsum, chalk or occasionally starch. Some very carelessly prepared samples which have a very poor appearance are coated with a well-prepared blue, so that it is necessary to make more than a superficial examination. The adulterants usually met with can be detected in the ordinary manner, and if the sample be examined in the manner we have above described any sophistication will be revealed.

Although largely employed, and of great value, Prussian blue is not quite permanent in its nature. This is much more marked in badly prepared samples, so that any Prussian

blue employed for artists' work should be of the highest possible quality.

We have again recently come across samples of Prussian blue which contained free potassium ferrocyanide. This is clearly due to imperfect washing, and in every case the pigment was very poor in colour, and when diluted with a white base more closely resembled a French grey than a good blue.

One of these had the composition—

Moisture	3·71
Prussian blue	89·29
Water-soluble matter (alkaline ferro or ferricyanides)	7·00
	100·00

The presence of so much ferrocyanide is not only evidence of incomplete washing, but also clearly shows that ferric chloride was not used as an oxidising agent for the Everitt's salt. The finest colour we have examined was one prepared by oxidation with this reagent.

Two samples of Prussian blue, ground in oil, had the following composition :—

Oil	9·96	24·61
Prussian blue	42·24	26·00
Calcium carbonate, etc. . . .	25·80	27·13
Insoluble in acid ($BaSO_4$) . . .	22·00	22·26
	100·00	100·00

These more closely approximate in composition to Antwerp blue, and it is certainly undesirable that such substances should be sold as Prussian blue without some qualifying description.

II.—NATURAL LAKES.

This important group of pigments may be regarded as compounds of some animal or vegetable colouring matter with an inorganic base. The usual metallic base employed

in their preparation is alumina, or a mixture of that body with lime, magnesia or oxide of iron.

The old-fashioned lakes were prepared from such sources entirely, the colour being derived from either an insect, such as cochineal, or a plant such as logwood. To-day, however, lakes are prepared from the coal-tar colouring matters, and thus differ from the older lakes in the fact that their colour principle is of artificial origin. Although frequently of very beautiful colour, the lakes as a class suffer from one common objection, which restricts their use, namely, the fact that they are not permanent to light. They were used in very early times, the Italian artists being very fond of them. The origin of this class of colouring matters is said to be as follows: In the early days of Italian dyeing, a colouring material was used which was known as "lac". In the process of dyeing it was necessary to use a substance as a mordant to develop and fix the colour on the fibre, and salts of aluminium and tin were soon found to be the most suitable for the purpose. During the process, combination naturally took place in the vat liquid itself as well as on the actual fibre. As a result the insoluble compound of colour and base, which was of a very voluminous nature, floated to the surface in the form of a scum. This was collected and dried, and then sold to artists under the name of lacca. This special name soon became generic, as other colours were found to yield similar compounds, and so the name passed into common use. As would be expected, in certain well-defined cases the natural colouring matter is of an acid nature, which accounts for its ready combination with bases. This will be referred to in more detail in the sequel, but at the present moment it may suffice to say that a "theoretical" lake would consist of a compound between the acid and the base in molecular proportions: such theoretical lakes, however, have no practical existence, and often a series of lakes

of a given colour exists, in which the tint depends entirely on the proportion between the acid and the base, part of which is in chemical combination, and part in a kind of mechanical mixture. Although the processes used for the preparation of these colours vary very much, and are often carefully kept secret, the principle underlying their preparation may be illustrated in the following example. A decoction of the natural substance in water is prepared of as high a strength as possible, and after filtering it from suspended particles, a solution of the base is added to the liquid. The exact conditions under which the base is added determine the resulting tint, and it is in a scientific appreciation of these conditions that success depends. Some natural colouring matters exist ready formed in the plant, etc., and yield lakes which do not greatly differ in colour with the nature of the base used: whilst others do not exist as colours in the fresh plant, but are only developed when the base is added, and therefore differ greatly in the resulting colour of the lake, according to the nature of the base used.

Cochineal Lakes.

The Spanish conqueror, Cortes, and his comrades found the cochineal insect used in Mexico; and Prescott, the able historian of the conquest, seems to be definitely of the opinion that this was the first cause of the introduction of this colour into Europe.

The coccus used in Europe and Asia Minor was probably an insect, kermes, attacking the kermes oak (Quercus coccifera).

The beautiful colouring matter known as carmine, with its various lakes, is derived from the insect, Coccus cacti. The variety usually employed appears to be the dried fecundated female insect which has been reared on various species of Nopalea. It has been stated that so long ago as in the

time of Moses a red colour was derived from an insect, and used for dyeing the high priest's garment. This appears to have been some species of Coccus, probably identical with the Coccigranum of Pliny. The male insect does not furnish the colour.

It is true that this colour does not find a very extensive use except for a few special purposes, save in the dyeing industry. Its value as a pigment is greatly diminished on account of the action of light, possibly combined with that of moisture. Outside work in carmine colours, whilst being at first very beautiful, is not at all lasting. Further, it is naturally much more expensive than most reds, so that its use would be limited on that account alone.

The following preparations of this colour are, however, of sufficient interest and importance to justify their being shortly described.

Carmine.

It is uncertain when this beautiful pigment was discovered, but the earliest recipe that can be traced is one given by Homberg in 1656, when it was already a well-known colour. According to Wiegler (*Die natürliche Magie*, published in Berlin in 1782) it was accidentally discovered in Florence or Pisa by a Franciscan friar. It was said to have been thus found by chance during its use in the preparation of some medicine, in which form it had for some time enjoyed a reputation. Its name has even been derived from the same root as "carminative" by enthusiastic etymologists, assuming that its use in medicine was of this nature.

It may be regarded as the highest lake of the series to which it belongs, that is, it is the nearest approximation to a true compound without excess of base. The methods used in its preparation are varied, and have in most cases been kept as secret as possible. The following are some of the

published methods, but they must be accepted with reserve, as in many cases misleading information has purposely been published.

(1) One pound of crushed cochineal insects are boiled in 1 gallon of water for a quarter of an hour, and 1 oz. of ordinary alum added, the boiling being continued for a short time longer. After standing for a few hours the clear supernatant liquid is decanted, and this after a few days deposits about an ounce and a half of carmine. A crop of an inferior nature is deposited after a short interval. The addition of a little cream of tartar is said to assist in the deposition of the carmine. (2) Two pounds of the insects are boiled with water, and to the clear decoction, 2 oz. of alum and 3 oz. of a saturated solution of stannous chloride with 2 oz. of sodium carbonate are added, and the liquid allowed to stand for a time until the carmine is deposited. (3) The following method is the subject of a patent, dated 1856: 9 oz. of carbonate of sodium, 8 oz. of citric acid and 27 quarts of water are boiled together, a pound and a half of insects are added, and the whole again boiled for an hour and a half. The liquid is then strained and clarified. The clear solution is then boiled and 9 oz. of alum are added. After again boiling for five minutes, the fluid is allowed to stand, until the carmine is gradually deposited, when it is collected, washed and dried. Without suggesting that these methods will give the best results, it is not too much to say that they embrace the general principles underlying the successful preparation of carmine.

Pereira, about fifty years ago, stated that alum was no good as a precipitant for carmine, but that such a substance as chloride of tin must be used. This however is not in accordance with almost universal experience, since alum is found to be the base of most of the fine commercial carmines.

Carmine is a fine deep scarlet powder, of somewhat

variable tint, according to its quality, but always of a brilliant fiery brightness. The best quality of commerce is known as "nacarat carmine". It is insoluble in all the usual organic solvents, but is soluble in ammonia and the caustic alkalies. As a pigment it works well in oil or water, but is not permanent to light and air.

The Analysis of Carmine.—The moisture should be determined in the sample, and, so long as it is pure carmine, the value is of course proportional to the amount of dry pigment it contains. As a general rule, one does not expect to find more than from 15 to 18 per cent. of water in commercial samples. Over 20 per cent. may be regarded as an unfair addition. The ash should not only be determined, but it should be as fully examined as possible. The bulk of it should be alumina and lime, and there should be no insoluble white pigments present such as barium sulphate or siliceous matter. To determine whether excess of base in the uncombined state is present, the sample should be exhausted with dilute ammonia, which removes the true compound, and leaves the uncombined alumina and lime, together with some organic matter. Valuable information in regard to the colouring matter itself is obtained by boiling a few wool fibres for half an hour in the ammoniacal solution: aniline scarlet dyes a red-orange tint, whilst carmine gives a distinct purple red.

The presence of lakes of Brazil wood may be detected by dissolving the sample in the minimum quantity of very dilute ammonia and precipitating the carmine colour with excess of lime water. If Brazil wood lake be present, the filtrate after this treatment will have a purple or violet colour, as the colouring matter is not precipitated under these circumstances. A compound of Biebrich scarlet with salts of tin resembles pure carmine closely in colour and in general characters. If tin be present in the colour, this body should

be looked for. It may be detected by boiling white wool in the ammoniacal solution of the colour, when, if the scarlet be present, the fibre assumes a red-orange colour, instead of a pure red purple.

Dechan has given the following table of analyses of a number of commercial samples of carmine (*Pharm. Journ.*, 3, xvi., 511) :—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Moisture . .	22·1	16·1	2·0	22·3	20·2	23·5	10·0	21·2	13·0
Colouring matter .	46·1	69·2	34·1	65·7	60·8	69·5	72·0	18·4	67·5
Alumina and lime, etc. (dissolved by ammonia) . .	8·0	9·8	11·4	12·0	9·0	7·0	8·1	4·4	10·0
Organic matter (insoluble in ammonia) . .	21·8	2·5	18·5	—	9·8	—	8·0	52·4	9·5
Ash (insoluble in ammonia) . .	2·0	2·4	34·0	trace	0·2	trace	1·9	3·6	trace

Carmine is met with in commerce, adulterated with various aniline colours and occasionally with such substances as starch. Excess of mineral matter, generally uncombined alumina, is also met with, and according to Dechan (*Pharm. Journ.*, 3, xvi., 511) there are also found vermilion and chrome red. These adulterations are, however, we think, almost apocryphal.

Lafar (*J. prak. Chem.*, xliii., 130) has made a full analysis of a very fine sample of carmine (nacarat-carmine) and gives the following as his results. It contained 15·5 per cent. of water, 6·87 per cent. ash, 23·26 per cent. of nitrogenous matter and 52·37 per cent. of colouring matter. The composition of the ash was as follows :—

Cupric oxide	0·35
Stannic oxide	0·14
Alumina	40·48
Calcium oxide	44·20
Magnesia	0·61

Sodium oxide	5·40
Potassium oxide	3·20
Phosphoric acid	2·71
Silica	0·60
Carbonic anhydride	2·31
Ferric oxide	traces

In this, as in most cases, the ratio of the alumina to the lime and magnesia is practically that of one molecule of the former to two molecules of the latter. A very high-class sample examined by Liebermann was found to contain 17 per cent. of water, and yielded 3·7 per cent. of nitrogen, which may be taken as equivalent to about 23 per cent. of nitrogenous matter. The dry carmine contained 8·1 per cent. of ash, the composition of which was as follows:—

Stannic oxide	0·67
Alumina	43·09
Lime	44·85
Magnesia	1·02
Sodium oxide	3·23
Potassium oxide	3·56
Phosphoric acid	3·20

Neither the alumina nor the lime is precipitated from an ammoniacal solution of carmine by any of the usual re-agents, it being necessary to examine the ash to detect these metals.

Although the chemistry of the cochineal dye had been the subject of researches by John (1813), Pelletier and Caventou (1818), and by Preisser and Arppe, the earliest systematic study of the body may be regarded as that of Warren de la Rue, in 1847. He did not succeed in preparing the acid in a crystalline condition, and the formula which he assigned to it, $C_{14}H_{14}O_8$, must now be regarded as incorrect. Schutzenberger (*Ann. Chim. Phys.*, liv., 52) arrived at the conclusion that De la Rue's acid was a mixture of several bodies, and assigned to the pure acid the formula $C_9H_8O_5$. Schaller later (1864) analysed what he believed to be pure carminic acid and

assigned to it a formula differing from that of Schutzenberger's, only by containing one molecule more of water.

Hlasiwetz and Grabowsky (*Annalen*, cxli., 329) considered that carminic acid was a glucoside which yielded on hydrolysis a sugar and carmine red. Von Miller and Rohde, however, showed that this was not correct, as carminic acid did not alter on boiling with dilute sulphuric acid.

These chemists originally held the view that the acid was a naphthalene derivative, but have since modified their opinions. They consider that the formula of carminic acid is either $C_{24}H_{22}O_{14}$ or $C_{22}H_{20}O_{13}$.

The most modern researches, and those which are to be regarded as the most reliable, are those of Liebermann and of Schunck and Marchlewski.

Liebermann, who has recently devoted much attention to the chemistry of the cochineal dye, considers that carminic acid is an indene derivative of the formula $C_{22}H_{22}O_{13}$. The acid, which is easily soluble in water, readily passes into insoluble colouring matters, the change being accompanied by elimination of water and increase of molecular complexity. This change is characteristic of the bodies of the ketoindene series. On oxidation by potassium persulphate, the dye yields two other acids. These have been termed coccinic acid, $C_9H_8O_5$, a body very soluble in alcohol, but nearly insoluble in water, melting at 293° with decomposition: and cochinelic acid, $C_{10}H_8O_7$, which forms crystalline needles melting at 224° to 225°. It is moderately soluble in cold water, and easily so in alcohol. The former of these acids has been identified with the well-defined compound, hydroxy-uvitic acid. A study of these acids and their derivatives has led Liebermann to assign, provisionally, to carminic acid the constitution

$$\begin{array}{l} \mathrm{COOH,\ C_6H,\ CH_3(OH),\ CH,\ OH} \\ \qquad\qquad\quad | \qquad\qquad\quad | \\ \qquad\qquad\quad \mathrm{CH(OH)} \text{———} \mathrm{CH(OH).} \end{array}$$

Schunck and Marchlewski prepare pure carminic acid by treating cochineal extract with lead acetate, decomposing the lead salt with sulphuric acid in the presence of alcohol, and evaporating the liquid to dryness at the lowest possible temperature. The residue can be purified by dissolving in alcohol and precipitating with ether or benzene. It is then recrystallised from alcohol, when it forms small red prisms. Aqueous solutions of carminic acid, when evaporated, give an amorphous residue, but no crystals. According to Schunck, carminic acid possesses the formula $C_{11}H_{12}O_6$ or $C_{11}H_8O_4$ with two molecules of water of crystallisation. His preparation darkened at 130° and blackened without melting at 205°. In alcoholic solution it shows three ill-defined absorption bands, one in the green and two in the blue. The barium and calcium salts are brown, changing to violet with excess of base; the lead and aluminium salts are also violet, and the stannous salt scarlet. An aqueous solution is at once decolourised by animal charcoal, the latter increasing in volume and becoming gelatinous. This mass seems to be a compound which is not changed by alcohol, but is decomposed by alkalies. The anilide of carminic acid is deposited in ruby crystals from its solutions, and melts with decomposition at 189° to 190°.

Crimson Lake.

This pigment, which produces very beautiful results, is a more fully saturated lake of the colouring matter of cochineal than ordinary carmine. It suffers from the same defect as the last-named colour, namely, lack of permanency, so that its employment is somewhat limited. Much of the so-called crimson lake of the present day, however, is not a true cochineal colour at all; this is especially true of the pigment when used in oil, it then being generally supplied by the artists' colourmen of repute, made from the coal-tar product,

alizarin. When so made it has the advantage of being pretty permanent, but in chemical constitution it must not be confounded with the true crimson lake. When supplied as a water colour, it is generally made from the insect.

Crimson lake may be regarded as a more basic compound of carminic acid than ordinary carmine, with, of course, more or less foreign matter present as well. The following receipt has been given as producing a very fine shade of this exquisite colour: Twenty parts of the powdered insects are boiled with 400 parts of water and ten parts of cream of tartar. After filtration, a solution of 300 parts of alum and a small quantity of stannous chloride are added to the solution. The precipitate first formed is exceedingly brilliant, but the greater part of the colour is still in the solution. To effect its precipitation a solution of carbonate of sodium is cautiously added, when the alumina is completely precipitated, along with all the colouring matter. One can hardly fix any standard for the quality of this pigment, but it is necessary that it should be the product of the true cochineal, and it should, after allowing for the greater proportion of mineral matter, correspond closely in its behaviour with genuine carmine.

The following recipe is given by A. P. Laurie (Cantor Lectures, 1891) as from a MS. in the Library of the University of Padua, dated probably the middle of the seventeenth century.

"'*To make a most beautiful purple lake.*—Take an ounce of fine grana or cochineal, a quarter of an ounce of roche alum, and about a bocale full of common water. Boil the water with a quarter of an ounce of fennel seed until it is diminished one-third; then add the grana or cochineal finely pulverised, and boil the whole over a slow fire for a quarter of an hour; then add the pulverised roche alum, and let it boil for another quarter of an hour. After this, take it from the fire, strain it

through a linen cloth into a new and unglazed earthen porringer, and leave it there for eight days. You must then decant the water, or take it up gently with a sponge, evaporating the little which remains, until the colour is condensed, which you must afterwards keep in shells, adding to it a little lemon juice.'"

Mr. Laurie says: "I have tested this recipe, and find that a precipitate is thrown down of a purple colour. The addition of lemon juice referred to here, and in some other recipes, causes the lake to become more of a crimson and less of a purple."

Lac Dye Lake.

The substance known as lac dye is the product of Coccus lacca, an insect which lives on the banyan and other trees, especially those belonging to the genus Ficus. From the mature impregnated female insect a resinous exudation flows, which encloses the deposited ova. The twigs with the attached resinous matter and enclosed animal substance are broken off, and constitute stick lac. If the resinous mass be extracted with water, the greater part of the colouring matter present is dissolved, and the residue is known as seed lac, which when melted and strained and thus purified is sold as shellac. The colouring matter, or lac dye, is apparently prepared by treating the stick lac with a weak alkaline solution, and probably with a mixture of alumina and lime salts. It is used to only a very small extent now, and at most is only employed for pigmentary work in rare cases as an artist's colour.

The composition of this colour has been investigated by Schmidt (*Journ. Soc. Dyers*, etc., iii., 122), who called the chief constituent laccainic acid, and pointed out its close resemblance to carminic acid. He assigned to it the formula $C_{16}H_{12}O_8$, and described it as a brown-red crystalline powder

melting at 180°. It is soluble in alcohol and acetic acid, and to a fair extent in water. It is almost insoluble in ether.

It appears to be a dibasic acid, and the chief difference between it and carminic acid is the difference in the absorption spectra when dissolved in sulphuric acid. The two following analyses are given by Schmidt of two samples of the dye.

Moisture	9·0	11·26
Mineral matter	15·7	18·24
Colouring matter	10·4	13·2
Other organic matter	64·9	57·3

A good lac lake is prepared by the use of alum as a precipitant, and tin is also a good base when a fine colour is required. Samples of lac lake usually contain about 50 per cent. of colouring matter, 40 per cent. of resin, and 10 per cent. of alumina or of alumina and lime mixed.

Colours prepared from this dye are rather more permanent than those from cochineal.

Scarlet Lake.

This pigment used to be a mixture of crimson lake with more or less vermilion. The fugitive nature of the cochineal colour, however, has caused it to be replaced very generally by an alizarin colour. It thus becomes practically a permanent pigment.

Madder Lakes.

At one time the madder lakes were very largely employed, and held in very high esteem. Their value has in no wise diminished, but as the chemistry of the constituents of the root became more and more understood until finally artificial alizarin was an accomplished fact, the use of the natural product gradually diminished, until to-day it is almost entirely superseded by the artificial colours. Hence the

following short epitome of the chemistry of the madder lakes becomes of little but historical interest. The root of the madder plant (*Rubia tinctorium*) contains a considerable quantity of the colouring principle alizarin (*q.v.*) in the form of a glucoside which is known as ruberythric acid. This body has the formula $C_{26}H_{28}O_{14}$, and under the influence of either natural ferments or of dilute acids or alkalies it splits up into alizarin and the sugar, glucose. The equation representing this change is as follows:—

$$C_{26}H_{28}O_{14} + 2H_2O = 2C_6H_{12}O_6 + C_{14}H_6O_2(OH)_2.$$

The closely allied body purpurin (*q.v.*) occurs in the root in a similar condition.

The employment of madder has usually been in the form of a madder extract or of garancin, or garanceaux, the corresponding substance prepared from madder which has been once used and still contains some of its colouring matter. Garancin, obtained by treating the root with strong sulphuric acid, has been more frequently employed for the preparation of madder lakes than any other substance, and the following are the outlines of several processes which may be said to cover the general principles involved. Of course the details have been varied without limit, and lakes of different shades obtained accordingly. Khittel many years ago described the method he employed, in the following manner. One part of garancin is steeped in a solution of one part of sodium sulphate in thirty-six parts of water, and after a time is washed and pressed until all traces of the sulphate are removed. The purified garancin is then ready for use. A quantity of alum, free from the least traces of iron (which darkens the resulting lake very much), equal in weight to the garancin employed, is then dissolved in ten times its weight of water, and boiled. The purified garancin is then added to this solution. The mixture should not now be boiled, as the

resulting lake is darkened by too much heat. After about half an hour, with repeated agitation, most of the colouring matter is extracted. The liquid is then filtered from the residue, and when the filtrate has cooled to about 45° C. sub-acetate of lead is added in quantity equivalent to the amount of alum used. On stirring the mixture sulphate of lead is precipitated and rapidly subsides. The clear liquid is then decanted before it has time to cool. It is then heated for some time to nearly the boiling point, and then the first fraction of the lake separates. This is of a very fine red tint. After the first bright red lake has been deposited, the residual liquid is divided into two equal portions, and to one is added ammonium carbonate until a slight turbidity is apparent. The two portions are now again mixed, and again heated, when a fresh quantity of lake separates, which is not, however, so brilliant as the first fraction. Great care must be employed in drying these lakes, as heat injures them considerably.

Sace described the following method of obtaining a fine lake. He mixes 100 parts of an alcoholic extract of madder with 50 parts of water, and allows the mixture to macerate for twenty-four hours. More water is then added, and the solution is separated from the solid residue by straining through a silk sieve. A boiling solution of alum, containing 10 per cent. of the salt is then gradually added until precipitation takes place. The lake has a fine deep-red tint. By using sulphate of iron an almost black-violet lake results, whilst alum containing a little iron yields intermediate colours.

Kopp treated the root in powder with a solution of sulphurous acid and allowed the mixture to macerate for a time. The hot filtered liquid is then treated with a solution of aluminium acetate, or alum mixed with carbonate of sodium, and the lake precipitated in fractions. The finer tints are deposited first, the later fractions containing more and more of the accompanying impurities.

The high value of the natural madder lakes caused them to be often adulterated with cheaper colouring matters. The following description of the methods used for detecting the more usual adulterants is given by Chateau, and is reproduced from an interesting old treatise, *On the Manufacture of Colours* by Malepeyre. We give an account of the methods, but are unable to vouch that by following the directions there given one will be able to detect all the admixtures that may be present, although good indications of the purity of the lakes can undoubtedly be obtained in this manner.

"*Red and Pink Lakes of Madder.*—These lakes do not colour water, either hot or cold. They colour ether and alcohol only very slightly, and only after some time. By calcination they leave a residue of alumina.

"*Santaline.*—If the lake be dark it may contain santaline, the colouring matter of red sanders wood (*Pterocarpus santalinus*), which is detected by the orange-red colour acquired by the ether digested with the suspected lake. Alcohol under the same circumstances would be coloured red.

"If the lake be of a pink hue it may be falsified by lakes of Brazil wood or with (common) cochineal lakes. But as madder lakes and, generally, all lakes are insoluble in water, alcohol and ether, their colouring matter should be isolated, and the following method is proposed. Every lake with alumina for its base is soluble in hydrochloric acid, or in acetic acid to which a few drops of the former have been added, or in a solution of stannous chloride. After the lake is dissolved, ether is added to the solution, and the whole is shaken. All the colouring matter is dissolved in the ether, which will acquire the colour of the matter forming the basis of the lake.

"*Lakes of Brazil Wood.*—If the lake be mixed with a lake of Brazil, Pernambuco or Japan wood, the colouring matter

will be dissolved in the ether by the above process, and the ether will be of a golden-yellow colour.

"*Venice Lake.*—This lake, one of the finest of the Brazil wood lakes, will disengage ammonia if heated in a test tube with a solution of potash. A pure madder lake does not yield any ammonia under these circumstances.

"*Carmine Lake.*—Water will be coloured if cochineal lake is present, and the colour is intensified by heating. Aqueous solutions containing cochineal lake become violet when soluble alkalies are added, and give a violet precipitate with lime water, stannous chloride or zinc salts. Cochineal lake is turned a cherry red by stannous chloride, and the solution stains paper. Madder lake does not behave in this manner.

"*Campeachy Lakes.*—In the presence of these lakes the addition of hydrochloric acid produces a crimson red coloration. When extracted with ether as above mentioned, the ether will be of a golden-yellow colour, which yields the crimson red reaction with hydrochloric acid.

"*Alkanet Lakes.*—The lake is dissolved in acetic acid and the solution extracted by carbon bisulphide. If alkanet be present, the carbon bisulphide is coloured an intense violet red. This is characteristic of this colouring matter. When heated, the lake gives off violet fumes if alkanet be present. After dissolving the lake in acetic acid, and separating the colour with ether, this is evaporated, and the residue is treated with alcohol, which dissolves the colouring matter of alkanet. The alcoholic solution gives a blue precipitate with lead subacetate solution.

"*Orchil.*—If orchil colouring matter be present, the colour is yielded to hydrochloric as a deep red. If this solution be shaken with ether, the orchil does not yield the least colour to that solvent.

"*Prussian Blue.*—In the case of this somewhat rare adulterant, the lake will be of a violet colour. This will be

changed to a green by hydrochloric acid, and the iron cyanide compounds can be recognised and determined by the usual methods (see Prussian Blue)."

Alizarin Lakes.

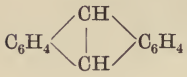
The chemistry of this group of pigments is now of very great importance, since the alizarin colours have practically replaced the madder colours for dyeing purposes, and have of recent years become of great importance as pigments for certain kinds of work. In the dyeing industry they are always employed in such a manner that they yield lakes as the resulting compound, so that alizarin dyes differ but little in theory from alizarin pigments.

Alizarin may be described as an anthracene derivative, and as the number of colouring matters derived from this coal-tar hydrocarbon is very limited, and since they all resemble each other very closely in their chemical properties, the anthracene group may be looked upon as an isolated and naturally related series of coal-tar colours.

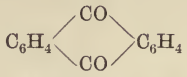
They are of a strongly acidic nature, which explains the fact that they form admirable lakes, and in dyeing they can only be used in conjunction with mordants, or, in other words, can only be employed in the form of lakes. They possess the advantage of being very permanent to light, far more so than most coal-tar colours, and they are also very fast on fibres when used as dyes.

Commercial alizarin.—The hydrocarbon anthracene is usually transformed into alizarin by means of three distinct operations. It is first oxidised to anthraquinone by means of chromic acid, and the resulting body is treated with sulphuric acid in order to convert it into a mixture of sulphonic acids. These are melted in the last stage of the process with caustic soda, when alizarin is produced. These steps in the

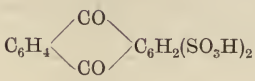
transformation are illustrated by reference to the following diagrammatic formulæ :—



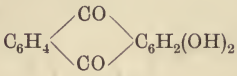
Anthracene



Anthraquinone



Anthraquinone di-Sulphonic Acid



Alizarin

Alizarian is, chemically, 1 : 2 : dioxy-anthraquinone. It forms orange-red needles melting at 290°, and subliming at higher temperatures. It is identical with the principal colouring matter of the madder root (*Rubia tinctorium*), in which it occurs as a glucoside known as ruberythric acid (identical with morindin, from *Morinda citrifolia*).

Of the trioxy-anthraquinones, of which a number are known, the most important are purpurin, flavopurpurin and anthrapurpurin. These are all isomeric bodies related to alizarin by having one of the hydrogen atoms (different in each case) replaced by an OH group.

Alizarin, $C_{14}H_6O_2(OH)_2$, is prepared in the pure state by melting pure anthraquinone-monosulphonic acid with caustic soda. It can also be obtained from ordinary blue shade commercial alizarin paste in the following manner. The paste is dissolved in caustic soda, and the solution filtered. A solution of barium chloride is added, and the whole is heated to boiling point, when the barium compound of alizarin separates out in a crystalline condition. This is collected on a filter and washed, and finally decomposed by an acid. It can be freed from the last trace of impurities by recrystallisation from glacial acetic acid or by sublimation. Alizarin has also been obtained synthetically by several methods, but these are not necessary to record here. Pure alizarin forms fine

orange-red crystals melting at 290°. It is almost insoluble in cold water and only slightly so in hot water, one litre dissolving 0·31 gr. of alizarin at 100°. It dissolves in sulphuric acid with a red-brown colour, but on dilution the alizarin is precipitated in an unchanged state. When crystallised from moist ether, alizarin contains three molecules of water of crystallisation. If precipitated by acids from alkaline solutions, it also contains water, which is driven off at 100°. Alizarin behaves towards alkalies as a weak acid. It dissolves in caustic alkalies and in ammonia with a blue-violet colour, but is precipitated from such solutions by dilute acids. With calcium and barium salts, alizarin forms violet precipitates, and with all other bases it yields practically insoluble lakes. Those of alumina and tin are red, the others mostly of a darker colour. Towards these bases alizarin behaves as a strong acid, displacing even hydrochloric and nitric acids from their combinations.

In commerce alizarin is always sold as a paste, which contains the hydrates of alizarin and the allied colouring matters in a fine state of division. The average quantity of dry colouring material in these pastes is about 20 per cent., but sometimes as much as 60 per cent. is met with. The two most important commercial shades are those known as alizarin blue shade (alizarin V) and alizarin yellow shade (alizarin G). The blue shade results when the sulphonation of the anthraquinone has not been carried beyond the monosulphonic acid stage. The yellow shade contains little true alizarin, but mostly anthrapurpurin and flavopurpurin. The latter body is responsible for the yellow shade, the former yielding a neutral red with alumina.

Purpurin, $C_{14}H_5O_2(OH)_3$, which is found associated with alizarin in the madder root, crystallises with one molecule of water, and melts at 253°.

Anthrapurpurin (isopurpurin) has the same empirical

formula as the last-named body, merely differing from it by the orientation of the (OH) groups. It melts at 360°.

Flavopurpurin is also isomeric with purpurin, and melts at above 330°. From the above brief descriptions of the properties of the colouring matters of the alizarin group, it will be easily understood how very numerous shades of lakes are produced from them, many of these differing greatly in tint, whilst being but slightly different in chemical composition. Of the varieties of these lakes, the following are best known as commercial pigments: alizarin carmine, scarlet lake, burnt carmine, Indian lake, permanent crimson, permanent violet, purple lake, sap green, olive green, olive lake, and others known under various fancy names.

The chemical composition of these pigments cannot be regarded as regularly constant, but as far as possible this is indicated in the following paragraphs, in which a description of the chief well-defined compounds of this nature is given.

Pure alizarin yields, as above mentioned, with calcium and barium salts a series of violet lakes, which vary slightly in tint according to the conditions under which they are formed. With tin and alumina it yields good red lakes, but with other bases the lakes are dark in colour. The slightest trace of iron salts suffices to change the alumina red to a dull red or even to a brown colour. When the commercial alizarin is employed, the tint of the resulting lake necessarily depends on the exact composition of the alizarin. Ordinary alizarin red is the alumina lake of the yellow shade of alizarin, that is, it contains a large quantity of the trioxyanthraquinone lakes. Alizarin pink is prepared from the blue shade, and contains more of the true alizarin compound. They can all be obtained by dissolving the colouring matter in an alkali and precipitating the lake by a solution of alum. By varying the base or by using a mixture of tin and alumina, for example, different shades are obtained. According to recent researches

of Liechti and Suida the composition of the normal alumina-lime alizarin red lake is Al_2O_3, CaO, $(C_{14}H_6O_3)_3$, H_2O. Traces of ferrous salts change the colour to a violet, and with ferric salts the darkening is very pronounced, a brown being often produced. A small quantity of chromium salt is sufficient to change the alumina red into a fine puce colour.

In addition to the lakes of alizarin and its oxy compounds, those of the sulphonated derivatives have a considerable importance.

To prepare alizarin-sulphonic acid of the degree of sulphonation required for general work, one part of alizarin is acted on by three parts of strong sulphuric acid containing about 20 per cent. of free sulphuric anhydride, at 100° to 150°. The heating is continued until a sample dissolves completely in water. The reaction product is then dissolved in water and the excess of sulphuric acid is removed by treatment with barium or calcium hydroxide, and the filtered liquid is evaporated, when the necessary alizarin-monosulphonic acid is obtained. The free acid is soluble in water, and yields three series of salts. Those of the general formula $C_{14}H_5O_2(OH)_2SO_3R$ are yellow or orange and are soluble in water. The sodium salt is the commercial product used for the preparation of many of the colours. The alkali salts of the general formula $C_{14}H_5O_2(OH)(OR)SO_3R$ are of a red-violet colour, and those of the alkaline earths of a red-yellow colour. Those salts where the three available hydrogen atoms have been replaced, of the formula $C_{14}H_5O_2(OR)_2SO_3R$, are the most soluble, and are of an intense violet colour.

The acid forms excellent lakes, as would be expected from its marked acidic properties, and the aluminium lake is of a deep carmine colour. It forms the basis of the most permanent of the crimson colours, and is known as "permanent crimson" or "alizarin carmine". With tin salts as the base of the lake, orange shades are obtained.

Fine colours belonging to the series of lakes can also be prepared by the use of nitro-alizarin. Two mononitro derivatives of alizarin are known, that termed the β-variety being the most generally employed. This is obtained by treating the blue shade of alizarin in a fine state of division with nitrous fumes. The purified nitro compound has the formula $C_{14}H_5O_2(OH)_2(NO_2)$ and forms soluble red-coloured salts with the alkalies. With alumina it yields a fine insoluble orange, and with iron salts a red violet.

An alizarin blue is known, but it has not been used to any great extent for pigment work. Several closely allied varieties are recognised, but even the best of them is not so fast to light as indigo, and is not fit to replace the latter. The alizarin blues are yielded by heating nitro-alizarin with glycerine and sulphuric acid, and appear to be quinoline-alizarin compounds. Green colours are now used prepared from alizarin. These are those sold under the names: sap green, olive green and olive lake. Alizarin green is formed by treating alizarin blue with a large excess of fuming sulphuric acid, and subjecting the resulting product to the action of either alkalies or acids. The colour thus obtained is known as "alizarin blue-green," and if it be heated to 130° with concentrated sulphuric acid alizarin green is formed, which, after separation and washing with water, forms fine blue-grey needles. As seen in commerce, however, it is a red-brown solution of the colour, which smells of sulphurous acid and when boiled gives a blue precipitate. This is used for dyeing purposes and is usually mordanted with potassium bichromate.

For the detection of alizarin colours a spectroscopic examination is most useful, as they all give more or less characteristic absorption bands which should be compared with those yielded by colours of known origin. The alizarin colours may be distinguished from madder colours by boiling them with a solution of aluminium sulphate. In the latter

case the solution is strongly fluorescent. Concentrated mineral acids remove the base from the lake, and the free acid may then be examined. Bleaching powder destroys the colour of most of the alizarin compounds, but in some cases very slowly, especially in the case of the most permanent reds. None of them can, however, withstand the simultaneous action of an acid and chloride of lime.

Campeachy Lakes.

The Campeachy lakes, as they are usually called, are lakes prepared from logwood (*Hæmatoxylon campechianum*), a tree abounding in the West Indies, Mexico and, generally, in South America. When felled, the wood of the tree is nearly colourless, but it soon assumes a dark reddish-brown colour, which is deeper on the surface of the wood than in the interior. It is evident, therefore, that the colouring principle is the result of a chemical change after the felling of the wood; but whether this is merely an oxidation process, or is at the same time accompanied by the hydrolysis of a pre-existing glucoside is not a matter of certainty. It appears most probable that the glucoside is in the first place split up into a sugar and hæmatoxylin, and that the latter is afterwards partially oxidised to hæmatin. An aqueous extract of the wood is a well-known commercial article, and whether used as a dye-stuff or for the precipitation of lakes, it is important that the evaporation of the water be conducted at as low a temperature as possible, and that oxidation be not allowed to proceed too far. The fermentation, as it is called, of the wood, by which the glucoside is decomposed with the formation of hæmatoxylin, takes place best when the wood is rasped into thin shavings and moistened.

Hæmatoxylin, $C_{16}H_{14}O_6 + 3H_2O$, the initial active principle of logwood, crystallises in yellowish prisms having a sweet taste. It is very soluble in water and in alcohol, and also in

alkalies. It can be obtained by treating the aqueous extract of logwood, or the powdered wood itself, with ether, and evaporating the liquid to a syrup, adding water and allowing it to stand for several days. The hæmatoxylin, in a fair state of purity, is gradually deposited, containing three molecules of water of crystallisation if in the prismatic form, but only one if it occurs as fine granules. By heating to 100° a portion of the water is driven off, but a higher temperature is required to drive off all of it. Hæmatoxylin is not very soluble in *cold* water, but is easily so in hot water, alcohol, ether and carbon bisulphide. It contains several hydroxyl groups, and forms several well-defined methyl and acetyl derivatives (*Monatshefte*, xv., 139). It behaves as a weak acid, dissolving readily in solution of ammonia and caustic alkalies. These alkaline solutions are, when perfectly fresh, almost colourless, but they rapidly absorb oxygen from the air, with the formation of oxidation products, amongst which the most typical is hæmatin, and at the same time becoming bluish, then a deep red-brown. The more or less pure alkaline compounds can be prepared by "salting out" the alkaline solutions. Lead acetate gives with hæmatoxylin a bluish white precipitate, rapidly darkening on exposure to the air. Tin salts produce a permanent rose-coloured precipitate sometimes used as a pigment. Ordinary alum gives a bright red colour, and aluminium acetate a fine purple; there is only a slight precipitation, however, unless other salts are present to assist.

Hæmatoxylin is very sensitive to alkalies and to acids, being used as an indicator in chemical analysis. With free alkalies it yields a bluish colour, while with acids it is red. It is especially sensitive to ammonia and to calcium carbonate. Hence it is not to be regarded as a very permanent pigment, so far as its initial shade is concerned. Chalk should never be used as a diluent.

Hæmatein, $C_{16}H_{12}O_6$, is easily produced from hæmatoxylin by atmospheric oxidation, especially in the presence of an alkali. It may be rapidly prepared by saturating an ammonia solution with hæmatoxylin, and allowing it to stand exposed to the air. Hæmatein-ammonia, $C_6H_{11}(NH_4)O_6$, is formed, from which acetic acid precipitates free hæmatein. This body is a reddish-brown powder with a metallic lustre of a greenish hue. It is sparingly soluble in cold, but more easily so in boiling water. It is only slightly soluble in alcohol and acetic acid, and not very soluble in ether. Alkalies, however, dissolve it with avidity, the solution being at first blue or purple, but on oxidation by the air it darkens considerably, becoming of a deep brown colour.

It forms a well-defined ammonium salt, which occurs as a deep violet powder consisting of microscopic prisms, which dissolve in water with a purple, and in alcohol with a red colour. At 100° the ammonia is volatilised, or even at ordinary temperatures in a vacuum over sulphuric acid. With copper sulphate its solution gives a violet-blue precipitate, and with stannous chloride a violet precipitate. It reduces silver nitrate. By reduction with sulphurous acid a portion at least of the body is converted into hæmatoxylin. A sulpho acid is obtained by treating it with cold concentrated sulphuric acid, and is precipitated as an orange-red crystalline powder by adding acetic acid to the sulphuric acid solution. It has the formula $C_{16}H_{11}(SO_3H)O_6$.

The reactions obtained from preparations of logwood are due to the simultaneous existence of hæmatoxylin and hæmatein. Dilute acids turn the colour yellow, but excess of strong acid gives a red colour. Sulphuretted hydrogen decolourises the solution, and sulphurous acid turns it yellow. Alkalies give at first a red, then a violet and finally a brown colour. Lime, barium and most of the heavy metals produce characteristic precipitates.

Stannous hydroxide gives a well-defined violet lake, whilst stannic salts behave as acids, turning the colour red. Salts of iron yield a blue-black colour, so deep that the iron compounds of logwood are employed with great success as inks. Mercuric salts give an orange, antimony salts a carmine, and bismuth salts a violet precipitate. Alum gives at first a yellow colour, which becomes red after a time: while aluminate of sodium gives a blue-violet precipitate insoluble in excess of alkali.

This reaction is said to be so delicate that logwood colour may by it be detected even when mixed with other colours. Another very well-defined test is the colour produced by bichromate of potassium. This test is best applied by boiling a piece of wool in a solution of potassium bichromate, and then immersing the wool in the colour decoction. In the presence of logwood it will be dyed an intense black.

To isolate the colour principles the lake is acidulated and the acid aqueous liquid is shaken with amyl alcohol. The alcoholic liquid is then extracted by a solution of borax. To purify the colour, the borax solution is rendered acid and the colour again extracted with amyl alcohol, and the solvent evaporated.

The best defined of the lakes of this important colour (which, however, find their chief employment in the dyeing industry) are the following:—

Aluminium salts yield deep violet-grey shades, varying according to the exact method of treatment adopted in the manufacture. Ferrous salts give blue-black lakes of great intensity, whilst numerous varieties are produced by using a mixture of the two metals. With chromates, logwood decoctions yield black colours which gradually turn green on exposure to light. By the use of potassium ferricyanide, etc., in dyeing operations, very fine and permanent deep blue shades can be obtained.

In the examination of the logwood lakes the following points are to be noted. If to the lake a few drops of concentrated hydrochloric acid be added, the colour produced is a cherry red. A spot of this is absorbed by blotting paper, and touched with a solution of aluminate of soda, which at once turns it blue. The blue and violet lakes leave on ignition an ash consisting of alumina or alumina and iron oxide, or the base may consist almost entirely of oxide of tin. The black lakes leave an ash containing alumina with a large amount of iron oxide, or, more usually, chromium or copper oxide. Free chlorine (treatment with bleaching powder) readily bleaches all logwood colours. By boiling with glacial acetic acid, the colouring matter is dissolved, the acid having a rose-red colour, changing to yellow on heating. On adding ether and then sufficient water to cause the ether to separate, any indigo present will be found either in the ether or at the junction of the two layers, whilst the logwood will be present in the lower layer, colouring it a reddish-blue. If the colour is not very pronounced, a few drops of hydrochloric acid are added. The aqueous layer will then be a fine red colour.

Quercitron Bark Lakes.

Amongst the natural yellow colouring matters, all of which are of vegetable origin, the most important are the lakes prepared from the bark of *Quercus tinctoria* or "black oak," which is found abundantly in the southern parts of the United States. The bark itself is a regular commercial article, usually appearing in the market as a mixture of fibres and coarse buff or yellow powder. A more concentrated form of the colouring matter is that known under the name "flavin," which is a preparation obtained by treating the bark with sulphuric acid (somewhat analogous to garancin), and which contains a large proportion of the colouring principle of the bark, quercitrin, together with its decomposition pro-

duct quercetin. "Aurantine" and "patent bark" are similar preparations.

Quercitrin, the active colouring principle of the bark, is a glucoside, about the constitution of which much discussion has arisen. It may be prepared in a state of purity by treating the coarsely powdered bark for six hours with 85 per cent. alcohol at boiling temperature. The alcohol is recovered from the extract, acetic acid is added, and a great deal of the extraneous matter is precipitated by the addition of an alcoholic solution of acetate of lead; the excess of the latter reagent is removed by sulphuretted hydrogen, and the filtered liquid is evaporated to dryness. The residue is dissolved in alcohol, and the filtered solution precipitated by the addition of water. The quercitrin is mostly thrown down by this, and is purified by recrystallisation from boiling water.

Quercitrin crystallises from water or dilute alcohol in small yellow glancing needles or tablets. It is easily soluble in absolute alcohol, slightly so in cold water, but more so in hot water. It is nearly insoluble in ether. When anhydrous it melts at 169° and at higher temperatures is decomposed with the formation of—*inter alia*—quercetin. The air-dried preparation, containing possibly a molecule of water of crystallisation, melts at 173° to 176°. A solution of quercitrin is coloured an intense green by ferric chloride solutions.

Its solutions are precipitated by lead acetate, but not when much free acetic acid is present. It easily reduces silver and gold salts in the cold. Quercitrin is easily dissolved in alkalies, the solution however soon becoming brown on exposure to the air.

Liebermann has assigned to it the formula $C_{36}H_{38}O_{20}$, but the more modern researches of Herzig (*Monatshefte f. Chem.*, xiv., 58) strongly support the formula $C_{21}H_{22}O_{12}$ or probably $C_{21}H_{20}O_{11} + H_2O$. By the action of boiling dilute sulphuric acid the body, which is clearly a glucoside, splits up into

quercetin and the sugar rhamnose. Assuming the formula to be $C_{21}H_{20}O_{11}$, when anhydrous the reaction may be expressed as follows:—

$$C_{21}H_{20}O_{11} + 2H_2O = C_6H_{14}O_6 + C_{15}H_{10}O_7,$$

the products being hydrated rhamnose and quercetin.

According to Wachs, the so-called quercitrin found in numerous other plants, such, for example, as *Thuja* and *Sophora*, is a compound of quercetin with one molecule of rhamnose and one of glucose, thus differing from normal quercitrin by containing an extra molecule of sugar.

At all events no less than four well-defined glucosides which yield quercetin on hydrolysis have been described. These are (1) quercitrin, which yields on hydrolysis one molecule of rhamnose; (2) rutin, which occurs in ordinary rue, and yields two molecules of rhamnose; (3) Viola-quercitrin, which is extracted from the flowers of *viola tricolor* and yields dextrose on hydrolysis; and (4) osyritin, from a Cape sumach, *osyris compressa*, which yields dextrose, but in different proportion to (3).

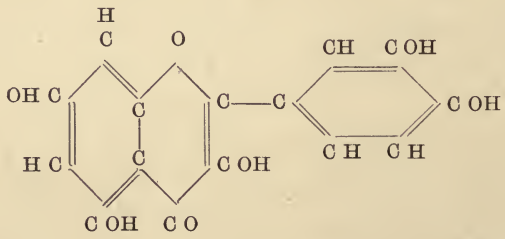
Quercetin, the product of the hydrolysis of quercitrin, forms a yellowish-gold crystalline powder, which is insoluble in cold and only very slightly soluble in hot water.

W. H. Perkin recommended the following method for the manufacture of quercetin. The bark in powder is washed with salt solution to remove impurities, and then extracted with cold dilute ammonia. The extract when neutralised with dilute sulphuric acid, deposits a brown amorphous precipitate containing little or no colouring matter; this is filtered off, and the clear lemon-yellow solution which contains the glucoside quercitrin is acidified and boiled, when crystals of quercetin soon begin to separate. These are collected while the mixture is still warm, in order to prevent their contamination with a brown flocculent matter which after-

wards separates. The nearly pure quercetin can be completely purified by recrystallisation from dilute alcohol. It is almost insoluble in ether. By rapid heating it melts at about 250°, or when anhydrous, according to Wachs, at 299°. At higher temperatures it sublimes, part being decomposed and part undecomposed. The alcoholic solution gives an intense green with ferric chloride solution, the colour changing to dark red on warming. Acetate of lead gives a red precipitate. Silver and gold salts are easily reduced in the cold by it, and copper salts when boiled with it in solution. Corresponding to Liebermann's old formula for quercitrin, $C_{24}H_{16}O_{11}$ has been assigned to quercetin, but in the light of modern researches there appears no doubt that $C_{15}H_{10}O_7$ is the correct formula.

Quercetin has been obtained by Perkin and Pilgrim (*Journ. Chem. Soc.*, 1898, 267) from the Indian dye-stuff asbarg (*Delphinium Zalil*), but the nature of the glucoside with which it was probably in the first instance associated has not been determined. It also occurs to a small extent in the root of *Podophyllum emodi* (Dunstan and Henry, *Journ. Chem. Soc.*, 1898, 209), and also in the leaves of New South Wales sumach (*Rhus rhodanthema*), and in various other plants, such as the catechu-producing trees.

The most probable constitution of quercetin, which is supported by a great deal of experimental work, is



Perkin (*Journ. Chem. Soc.*, 1896, 1447) has shown that

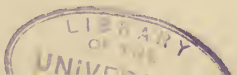
quercetin and its allies (such as fisetin, rhamnetin, etc.) form well-defined additive compounds with acids. This property may possibly be of use in enabling one to distinguish between this group of natural yellow colours and all other groups. For example, a saturated boiling solution of quercetin in acetic acid yields, on the addition of a few drops of sulphuric acid, a glistening mass of yellow hair-like needles. On separation and washing with acetic acid and drying at 100° they are decomposed quantitatively by water into sulphuric acid and quercetin.

The lakes of these coloured principles are usually made with an aluminium basis, the precipitate being of a very beautiful yellow colour. No standard for the exact quality of such a lake can be laid down, but it is important to determine that the ash does not consist of a neutral body that has been used as a diluent.

If the compound be acidulated and the quercetin extracted with alcohol the solution will give a green colour with ferric chloride; if acidulated and treated with sodium amalgam it assumes a fine purple-red colour, and on concentration yields red prisms which dissolve in alcohol and a little free alkali with a green colour, the solution being rapidly reoxidised on exposure to the air. Some samples will allow of fairly pure quercetin being separated, which should then possess the properties given above. On fusion with caustic alkali, quercetin yields protocatechuic acid and phloroglucinol, which may be searched for.

Rhamnus Lakes.

The berries of various species of Rhamnus, including the common buckthorn, *R. cathartica*, yield green and yellow colours of some importance in dyeing, calico printing, and artistic work.



The following are used :—

Name.	Fruit of.	Description.
Persian berries (from Aleppo and Smyrna)	R. amygdalina R. oleoïdes R. saxatilis	Size of a pea, greenish yellow, hard shrivelled surface, divisible along well-marked depressions into four parts, each containing a triangular seed, bitter taste.
Avignon berries, graines d'Avignon (French berries)	R. infectoria R. alaterna	Smaller than above, only two seeds.
Spanish berries Italian berries Hungarian berries	R. saxatilis R. infectoria R. cathartica	Very similar to French berries.

Others are obtained from the *Morea*, *Wallachia*, and *Bessarabia*, but the real Persian berries are the most esteemed, and these especially when gathered in the unripe, yellowish-green condition, but not when they are pure yellow or brown to black.

When an aqueous decoction of Persian berries is allowed to stand, surface moulds grow, the liquid becomes ropy, and fermentation takes place, with the separation of a bright yellow insoluble powder.

Gellatly, and later Schützenberger, showed that these berries contained the glucoside xanthorhamnin. Liebermann and Hörmann showed that this, by boiling with dilute mineral acids, or by the action of the natural enzyme [1] of the berries, forms isodulcite and a colouring matter, rhamnetin. This latter was shown by Herzig to be a methyl derivative of quercetin (he believed it to be a dimethyl ether). Later he showed that quercetin was probably

[1] This enzyme rhamninase is precipitated by alcohol from the cold water extract of the fruit of *R. infectoria* as a pasty mass containing 28 to 50 per cent. of solid matter; it is very soluble in water, and its activity does not diminish appreciably on keeping. The dry substance contains 17 per cent. mineral salts, 53 per cent. substances coagulated by heat, and galactan. A temperature of 70° is most favourable to its action, which is destroyed at 85° (C. and G. Tanret, *Bull. Soc. Chim.*, 1899, iii., 21, 1073-75).

$C_{15}H_{10}O_7$, and rhamnetin probably $C_{16}H_{12}O_7$ ($= C_{15}H_9O_7CH_3$). Lefort, and later Schützenberger, showed that xanthorhamnin was not a chemical individual, and the latter chemist extracted two glucosides, *α*-rhamnegin (xanthorhamnin), yielding rhamnetin, and *β*-rhamnegin, yielding a colour more soluble in alcohol and acetic acid. Herzig extracted a glucoside yielding a colouring matter, the acetate of which melted at 169° to 171°, whereas acetyl-rhamnetin melts at 183° to 185°. This he separated by alcohol into rhamnetin and quercetin, and considered the glucoside to be a loose compound of xanthorhamnin and a glucoside of quercetin, which he named rhamnin.

Later, A. G. Perkin (*Journ. Chem. Soc.*, 1895, 496), who has done so much good work on natural colours, with J. Geldard took up the examination of Persian berries, and, allowing the orange-brown liquid obtained by soaking the ground berries (in a calico bag) with ten times their bulk of water to ferment, obtained a yellow powder, separated by the action of the enzyme, as was well known. When this precipitate no longer increased in quantity and had settled, the clear liquid was removed and the precipitate dried at 100°, and digested with boiling toluene. This gave a crop of brown needles agreeing fairly in composition with $C_{17}H_{14}O_7$, and melting at 214° to 215°—identical with *rhamnazin* prepared by these authors from a purchased rhamnus colour, "rhamnétine". The residue from the toluene extraction was crystallised from a large bulk of alcohol, and gave, on recrystallisation in alcohol and acetic acid, *rhamnetin*, $C_{16}H_{12}O_7$, M.P. above 280°, and sparingly soluble. The alcoholic mother liquors and aqueous main filtrate gave, on further treatment, minute yellow needles, readily soluble in alcohol and acetic acid, and crystallisable from ether and chloroform, agreeing in composition with quercetin, $C_{15}H_{10}O_7$, and yielding the characteristic acetyl derivative colourless needles, M.P. 189° to 191°.

The authors, in summing up, state :—

"These results are interesting, and show that xanthorhamnin, together with the unknown glucoside of rhamnazin, are readily decomposed at 40° by the ferment present in the berries. This, on the other hand, exerts but little influence on the glucoside of quercetin (quercitrin ?), which is also present.

"The colouring matters obtainable from Persian berries are therefore rhamnetin, or quercetin *monomethyl ether*, $C_{16}H_{12}O_7$, rhamnazin or *quercetin dimethyl ether*, $C_{17}H_{14}O_7$, and quercetin, $C_{15}H_{10}O_7$, itself."

They are of opinion that Schützenberger's β rhamnetin was quercetin.

Xanthorhamnin is prepared (Liebermann and Hörmann) by boiling for eight to ten hours powdered berries with three times their weight of 85 per cent. alcohol. On allowing to cool and stand for twenty-four hours a large quantity of impure glucoside, with a little free colouring matter, is deposited as a resinous mass. The clear solution allowed to stand for some days in a cold place deposits pure xanthorhamnin in pale yellow cauliflower-heads, and in such quantity as to render the liquid pasty. The total yield is about 12 to 13 per cent. By recrystallisation several times from alcohol, and then from alcohol with water and ether, it may be obtained in distinct crystalline needles. It does not crystallise from an aqueous solution. It is soluble in water and alcohol, but not in ether, benzene or chloroform. It should be dried rapidly over H_2SO_4 in a vacuum, but not by heat, as it melts at a low temperature when moist, but above 130° (it contains 2 molecules alcohol, which it loses at this temperature) when dry. The above authorities assigned the formula $C_{48}H_{66}O_{29}$ to xanthorhamnin. Both Fehling's solution and ammoniacal silver nitrate are reduced by it.

Normal lead acetate turns a solution orange, but the addition of ammonia precipitates an orange-coloured lake. Alcoholic KOH causes the separation from the alcoholic solution of a potassium derivative, $C_{48}H_{62}O_{29}K_4$. It is stated by Schützenberger that twelve acetyl groups can be introduced on acetylation; fusion with caustic potash causes formation of phloroglucin and protocatechuic acid, with an acid body giving an intense red colour with the alkali. Sodium amalgam causes the production of the former bodies, but not of the coloured body.

Mineral acids effect the hydrolysis of xanthorhamnin, but acetic acid does not, though the glacial acid be used.

The mixture of colouring matters known formerly as rhamnetin, the nature of which was indicated by Perkin and Geldard, is readily soluble in fixed alkalies, less readily in ammonia, and only slightly in alkaline carbonates. Its alcoholic solutions give a yellow precipitate with tin and alum solutions, a reddish brown with copper acetate, and an orange with lead acetate.

The behaviour of quercetin, rhamnetin and rhamnazin to acids is characteristic.

Quercetin easily forms a sulphate, hydrobromide, hydrochloride and hydriodide by addition of the acid to a boiling aqueous solution.

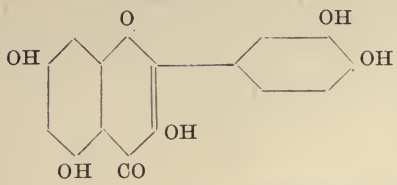
Rhamnetin forms a sulphate with difficulty, and no halides.

Rhamnazin requires a still greater excess of sulphuric acid to form an unstable sulphate, and forms no halides.

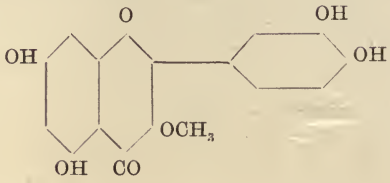
Those compounds are decomposed by water, and must be washed with acetic acid to free them from excess of mineral acid. In the case of the sulphates this must be done quickly.

This property of forming salts is, as previously mentioned, valuable in characterising the members of the quercetin group from one another and from other substances.

Adopting the quinonoid formula previously given for quercetin :—



rhamnetin becomes



while in rhamnazin a further hydroxy group is replaced by the methoxy group ; the addition of this group enfeebling the acid-combining power of the pigment.

Rhamnose (isodulcite), $CH_3(CH, OH)_4CHO + H_2O$. The sugar of xanthorhamnin melts at 93° when anhydrous, and at 122° to 126° when crystallised from acetone, and is also lævorotatory ; whereas the β modification has $a_D = \pm 10°$, and the γ variety obtained by warming this to 90° has $a_D = + 20°$, which after keeping goes back to + 10°.

Persian berries are used principally in calico printing.

A *steam yellow* is obtained by the addition of alum to the aqueous extract, thickening the lake with gum acacia and adding stannous hydroxide.

Steam orange is obtained by the use of stannous chloride and sodium acetate (equivalent of stannous acetate) as a mordant or lake base.

Steam green is prepared by the use of stannous chloride and alum with acetic acid and potassium ferrocyanide, and sulphuric or oxalic acid, gum being added to thicken (? should some iron salt be added to form Prussian blue and thus a green).

Persian berry carmine is a brown or yellow tin lake.

The colours known as brown pink and *stil de grain* are lakes produced from these berries.

These colours, generally speaking, are less fast and more expensive than those obtained from quercitron.

Sap Green.—The pigment known as sap green, used to some extent by artists, as are the Persian berry lakes, is prepared by fermenting the decoction of buckthorn berries (*R. catharticus*), lime water and gum acacia being added. After a week, alum is also added to the liquid strained from the berries, and the mixture concentrated by evaporation and the residue hung up in a pig's bladder to dry. This green buckthorn lake is mentioned by De Mayerne (1573-1655), a friend of Rubens.

A similar but poorer green is prepared from the black alder (*R. frangula*) and the evergreen privet.

An alizarin lake is also employed under the name of "sap green" (*vide supra*).

Lokao, Chinese green, is said to be prepared from the twigs of certain species of *rhamnus* (*R. chlorophorus* (*globorus*) and *R. utilis*) by boiling the bark with water and immersing cotton cloths, which take up a colourless substance, this turning green on exposure to air. The process is repeated until a quantity of colour has accumulated. It is then washed with cold water and boiled with water in which cotton yarn is laid. This takes up the colour, which is washed off and collected on paper.

Charoin of Lyons prepared a green from rhamnus bark by boiling it with water and adding lime water: on exposure to air in shallow vessels a green precipitate formed, which was increased by the addition of potassium carbonate. This seems more plausible than the reported method of the Chinese, and the product would appear to be a lake.

These greens, though of a rich colour, have not a good reputation for permanence.

The sap-green of a well-known firm of artists' colourmen was a chlorophyll-like looking colour, but as on ignition it left a blue ash discoloured by hydrochloric acid and containing about 36 per cent. silica, it was probably gamboge and ultramarine, a more permanent colour than real sap-green. This was an oil colour. Sap-green is usually used in water.

Brazil Wood Lakes.

Brazil wood is the product of *Cæsalpinia Brasiliensis*, a tree growing in the forests of Brazil. The red-dye woods known in this country under the names Sapan wood, Lima wood, Bahia wood, etc., are all products of various closely related trees of the same natural order, and take their names, as is evident, from the port of exportation. They all yield similar colours, but that from Brazil wood is the one which has been fairly thoroughly investigated, and whose chemistry is best understood. The colouring matter appears to be present in the form of a glucoside, which is probably identical in all the woods above named. It is decomposed by the action of a ferment in the presence of water, or by boiling with dilute acids, into glucose and the colouring matter, brazilin. This body is colourless itself, and appears to be closely related to hæmatoxylin, from which it differs in composition by only one atom of oxygen.

Brazilin forms white, shining needles of the formula $C_{16}H_{14}O_5$, and contains the equivalent of one and a half molecules of water of crystallisation. It is soluble in water, alcohol and ether: its solution on exposure to the air, especially in the presence of alkalies, is rapidly converted into a bright red fluid, from which acids precipitate the analogue of hæmatein, namely brazilein.

Brazilein, $C_{16}H_{12}O_5$, forms minute crystals of a greyish lustre, containing one molecule of water of crystallisation. It is formed from brazilin by several methods, such as the

interaction of the latter body with iodine, or by treating brazilin in acetic acid with potassium nitrite. A careful comparison of the brasileins prepared by the various methods has proved conclusively that they are all identical (*Berichte*, 23, 1428).

When powdered, brazilein is of a reddish-brown colour, and dissolves only slightly in cold, but more readily in hot water; the solution is of a yellowish-pink colour with a greenish-orange fluorescence. On the addition of an alkali the solution becomes crimson red, ultimately turning brown on exposure to the air.

Kopp has proposed the formula $C_{22}H_{18}O_7$ for brazilin, but the researches of Schall and Herzig have conclusively proved that the previously quoted formula is correct. A large number of bromine and alkyl derivatives have been prepared and described which all support that formula, for details of which the original papers must be consulted (see *Berichte*, 23, 1428; 21, 3009; 27, 524; *Monatshefte*, 15, 139; 14, 56).

The exact shade of the lakes formed from the extract of Brazil wood, in which form the colour is usually found, depends on the relative quantities of brazilin and brazilein present. Brazilein gives a good red lake with alumina, a greyish-violet to black with salts of iron, and browns with mixtures of the two. Stannic chloride gives a red, and there is also a lake of a fine dark crimson colour formed by the action of potassium bichromate. This appears to be due to the action of the chromic acid on the brazilin and brazilein, with a partial reduction to a lower oxide of chromium, which is of a basic character, and unites with the brazilein. Lead salts give a dirty blue lake. One of the most successful methods of obtaining these lakes is to pass a current of air through a solution of brazilin containing the requisite metallic salt, also in solution.

Brazilein and its derivatives can be reconverted into

brazilin and its derivatives by reduction by means of zinc dust.

If these lakes are pure, the residue left on ignition will be found to consist almost entirely of the metallic oxide with which the brazilein is combined. Sometimes starch or chalk will be found used as a diluent, but the use of the lakes is too small to cause much adulteration to be practised. Strong hydrochloric acid turns these lakes a pink colour, which is materially altered on dilution with water. Hypochlorous acid or chlorine rapidly bleaches them.

Alkanet Lakes.

Alkanet, as known in commerce, is the root—or portions of the root—of *Anchusa tinctoria*. It contains a red colouring matter of an acid nature which may be prepared by boiling the root with water in order to remove all soluble matter, drying it, and exhausting with alcohol. The alcoholic solution has a violet colour and is slightly acidified with hydrochloric acid, and evaporated to dryness. The dry residue is treated with ether, and this, on evaporation, leaves the red colouring matter in an impure condition as a dark red resinous mass.

This colouring matter was described so long ago as 1814 by Pelletier, who regarded it as a kind of fatty acid, and gave to it its name—anchusic acid. The formula assigned to it (old notation) was $C_{35}H_{20}O_8$. The same body appears to have been described by John (*Chemische Schriften*, iv., 85) under the name pseudo-alkannin, which he stated was present in the root to the extent of 5·5 per cent. The more recent investigations of Carnelutti and Nasisi (*Berichte*, 13, 1514) are the basis of our present knowledge of the active principle of the root. In preparing the acid, they exhausted the commercial extract of the root with a solution of potash, and from the alkaline solution they obtained an impurity present by shaking with ether. The potash solution de-

posits the alkannin, as it is now called, on being saturated with carbonic acid. It forms a dark red mass soluble in chloroform and acetic acid, but only sparingly so in other organic solvents. The formula assigned to the acid was $C_{15}H_{14}O_4$. A crystalline diacetyl compound was obtained by treating the acid with acetic anhydride and sodium acetate. A barium salt containing two atoms of barium to three molecules of alkannin was obtained by precipitating an alcoholic solution with ammoniacal solution of barium chloride.

Alkannin appears to be related to the red colouring matter of sanders wood. Liebermann and Römer (*Berichte*, 20, 2428) investigated the compound in 1887, and after a series of analyses they came to the conclusion that the formula of the acid was either that proposed by the above-mentioned chemists, or $C_{15}H_{12}O_4$. They consider that alkannin is a methylanthracene derivative, probably its dihydroquinone or its dihydride.

The alcoholic solution of alkannin is of a crimson colour, and is permanent to light and heat. It gives a blue colour with alkalies, and a blue-violet precipitate with aluminium salts, the acetate being the best to use for the preparation of the lake; a crimson precipitate with stannous chloride, and a purple precipitate with stannic chloride. Lead acetate gives blue, and iron salts violet, precipitates.

According to Allen, the best test for alkannin is an examination of its absorption spectrum. Its solution in amyl alcohol gives the best results, and exhibits three equidistant bands in the blue-green part of the spectrum. On adding ammonia to this solution, these bands give place to two fresh bands, one nearly coincident with, and the other on the red side of the D line. Bujard and Klinger (*Zeit. ang. Chem.*, 1890, 26) state that the alcoholic solution acidified with acetic acid gives a well-defined absorption spectrum, the three characteristic bands being as follows: the first is near and on the more

refrangible side of the D line; the second commences at E and extends to beyond b; and the third, which is faint, is close to F. On rendering the solution alkaline the blue solution shows two bands, one of which is midway between C and D, and the other commences at about D.

Alkannin resembles orchil (archil), but differs from the colouring matter of logwood, Brazil wood, etc., by being extracted from its ammoniacal solution by ether.

When natural madder lakes were articles of general commerce, adulteration of the latter with alkanet lakes was sometimes practised. A reaction said to be characteristic of alkanet lakes, and which was used to detect the presence of these bodies, was as follows: The lake was dissolved in acetic acid and the acetic solution was extracted with carbon disulphide; if alkannin were present the carbon disulphide solution was coloured an intense violet-red (see p. 210).

Santal-wood Lakes.

The wood of the so-called red sandal, *Pterocarpus Santalinus*, must not be confounded with that of the yellow sandal wood, *Santalum album*, from which the santal wood oil of pharmacy is distilled. Red sanders wood, as it is more frequently called, together with the woods of the allied trees which yield the so-called barwood, camwood and caliatour wood, are used for certain tinctorial purposes, but to-day the lakes from these woods are almost entirely superseded by coal-tar colours. They all appear to contain a colouring matter of the formula $C_{15}H_{14}O_5$, and it is probable that this is identical in all the woods. It is termed santalin. It appears to be an acid, but its chemistry is not well understood.

With stannous chloride the tinctures of the woods, especially those of santal and barwood, yield blood-red lakes, and

with ferrous salts a violet lake. A dark cherry-red lake is yielded by the use of tartar emetic.

Archil Lakes.

These lakes are now practically never used, as the coal-tar colours have superseded them, but the colouring matter is still used for other purposes, and a few lines treating of their general properties will not be out of place. Archil is the product of several species of lichens, of which the two principal are *Rocella fuciformis* and *R. tinctoria*. It comes into commerce as a paste or as a liquid. It is usually prepared by treating the finely chopped "weeds" with dilute ammonia, keeping the mixture at about 20° till a dark violet paste has been formed. This paste, when diluted with ammonia and filtered, yields "blue archil," and this, on gently heating to drive off the ammonia, yields the "red archil".

The pigment known as French purple is a lake obtained by treating the ammoniacal liquid with calcium chloride.

The pasty archil consists chiefly of ammonia combined with a colouring matter called orcein. This body owes its origin to the action of air and ammonia on the orcin present, in the same way as hæmatein is formed from hæmatoxylin. The lichens contain a considerable quantity of complex ethers, from the decomposition of which orcin results. The principal of these are the following:—

Erythrin (Erythric acid), $C_{20}H_{22}O_{10}$. This body when boiled with alkalies yields orcellinic acid and picroerythrin, the latter body being decomposed by further treatment into orcinol and erythrol, with the evolution of carbon dioxide. These reactions establish the constitution of erythrin as the diorcellinic ether of erythrol. Orcellinic acid is a dihydroxy-toluic acid, whilst erythrol is a tetratomic alcohol closely related to the sugars. The relationships of these bodies are shown in the following table:—

Orcinol . . . $C_6H_2(CH_3)(OH)_2H$ (methyl resorcinol).

Orcellinic acid . . $C_6H_2(CH_3)(OH)_2CO,OH$

Diorcellinic acid . . $\begin{matrix} O.C_6H_2(CH_3)(OH)CO,OH \\ CO.C_6H_2(CH_3)(OH)_2 \end{matrix}$

Erythrin . . . $C_4H_6 \begin{matrix} [OCO(OH)_2(CH_3)C_6H_2]_2 \\ (OH)_2 \end{matrix}$

Picroerythrin . . $C_4H_6 \begin{matrix} OCO(OH)_2(CH_3)C_6H_2 \\ (OH)_3 \end{matrix}$

Erythrol . . . $C_4H_6(OH)_4$

The special characters of these bodies are without interest for our present purpose.

Orcinol (Orcin) is a methyl-resorcinol, and therefore has the characters of a diatomic phenol. It occurs in the free state in several of the lichens used in the preparation of archil, but is chiefly a decomposition product of the above-described complex ethers which are present to so large an extent in the plants. It is a crystalline body melting at 58°, and on treatment with ammonia in the presence of atmospheric oxygen it yields the colouring matter orcein. According to Liebermann two compounds are formed, according to the conditions of the reaction. He states that if ammonia be in excess a body of the formula $C_{14}H_{12}N_2O_3$ results, whilst if the reverse be the case the compound has the formula $C_{14}H_{11}NO_3$.

The researches of Zulkowski and Peters (*Monatshefte*, 11, 227-245), however, have shown that the previous formulæ of these colouring matters are incorrect, and were based on the analysis of impure specimens. By careful procedure they obtained three distinct colouring matters from orcinol by the action of air and ammonia. They dissolved 50 grams of orcinol in 200 c.c. of water and added 200 c.c. of strong solution of ammonia. After standing for two months the mixture was examined and after a series of separations the orcein was obtained in the crystalline condition. It

forms a brown crystalline powder, of the formula $C_{28}H_{24}N_2O_7$, insoluble in water, but soluble in acetone, acetic acid, and alcohol.

French purple, as above stated, is a calcium lake of orcein, but finds very little employment now. If an archil lake be treated with hydrochloric acid and shaken with ether no trace of colouring matter will be dissolved, if the lake be made from pure archil. According to Slater, the presence of most other vegetable colours may be detected by treating 3 or 4 grams of the sample with 100 c.c. of water and 50 drops of a solution of stannous chloride. On boiling the liquid a yellowish colour will remain if the archil be pure, but if logwood be present a bluish colour will persist, and if most other red woods are present the colour will be reddish.

The colouring matter known as cudbear, or on the Continent as perseo, is obtained by the action of ammonia or urine on various lichens, such as *Lecanoria tinctoria* and *Variolaria orcina*, and is, therefore, very similar to orchil in its properties. The colouring matter of this substance appears to be either identical, or very closely related to that of archil, but sometimes the extract is considerably richer than that of the rocella lichens. Hence, it is frequently mixed with a considerable amount of mineral matter, usually common salt, not so much as a wilful adulteration as to bring the richer varieties down to one uniform standard.

III.—COAL-TAR LAKES.

The lakes produced from coal-tar colours have been indicated when dealing with the madder lakes, but in the present section it is proposed to deal with the lakes of the artificial colours at some length, as they have now assumed an importance which has gradually increased, with the

increase in our knowledge of the now universally employed coal-tar colours.

The natural colour lakes may, in general, be regarded as compounds of one or more natural colour acids with inorganic bases, with, at times, more or less mechanical admixture of excess of base or acid. Theoretically, however, the lake may be regarded as the true compound in the sense described.

In the same way the lakes of the artificial colours must be regarded as true chemical compounds, although the mechanical admixture plays an important part in the preparation of the colours in actual practice.

For the purposes of the present chapter, artificial colouring matters capable of forming lakes may be divided into three groups. These are as follows : (1) The artificial colour bases containing nitrogen in combination with hydrogen, so that the base behaves as an ammonia derivative. (2) Artificial colours of a purely acid nature, capable of combining with an inorganic base. (3) Artificial colours in which both acid and basic functions exist simultaneously in a well-defined degree. Such bodies may be typified by a sulpho acid of an amido compound.

In this sense then we understand a true lake, and it is necessary to here draw attention to the somewhat free use of the word "base" in connection with this subject. As we are employing the word, it refers to a compound or an oxide of a metal capable of uniting to form a definite compound with an acid. The word is also employed ("lake base," etc.) when referring to a neutral body, such as sulphate of barium or china clay, which is employed as an absorbent, or as a diluent for a colour, but in the present work the word will not be employed in that sense.

At the same time it must be admitted that the principles of lake formation are not altogether as well understood as one

could wish. Although we have emphasised the importance of recognising the principle of true chemical combination as the basis of the formation of lakes, there is considerable room for speculation as to the degree to which this combination is carried in a great number of cases which must be regarded as belonging to the class of true lakes. It is quite certain that advantageous precipitations of colour bases take place, when only a small proportion of the calculated molecular equivalent of the precipitating acid is used. This is especially the case when tannic acid is employed. Here, then, we have a case in which, whilst there is certainly a true chemical combination of the base and the acid, there exists in the compound far more base than the theoretical combination would require. It is usual to use the expression "mechanical combination" in such cases, and to escape from the difficulty of a lame explanation by the use of a term which is even more difficult to define than the original problem is to explain. In certain cases, where a voluminous precipitate, such as that of alumina in the hydrated state, is thrown down, a species of "mechanical combination" is not difficult to assume. For example, when one adds a solution of ammonia to a solution of alum mixed with a salt of calcium, a voluminous precipitate is thrown down. It is of such a bulky, gelatinous nature that together with the mass of water which assists to make up the "jelly," there is a considerable amount of lime salts: it is next to impossible to completely remove these lime salts by ordinary washing with water, and when the alumina is filtered off and dried, it will be found that there still remains an appreciable amount of lime in a state of intimate admixture with the alumina. But the quantity is not sufficient to explain the almost complete precipitation of a considerable excess of base by a small quantity of the precipitating acid, as in the case we have above quoted.

From a prolonged experience of compounds of the inorganic elements, which are more easily manipulated than the organic compounds from this point of view, we are acquainted with well-defined basic compounds, *i.e.*, compounds of a base with an acid which are not of normal constitution, but contain definite molecular proportions of the base in excess of that required for the normal compound. In our present imperfect state of knowledge concerning the exact nature of the combination existing between many organic compounds, it appears to us that the most feasible explanation of the somewhat erratic combinations of these lake bodies is the existence of an analogous series of compounds to those which, as just mentioned, are well recognised between inorganic elements. This, however, is merely a matter of speculation, and need not, therefore, be further discussed here. We now pass on to the consideration of the coal-tar lakes, and in doing this we have arranged the lakes in groups according to their colours, without taking their chemical constitution into consideration, a practice which, as evident in the earlier chapters, would not have been convenient when dealing with the pigments of inorganic origin.

Red Lakes.

By careful manipulation practically any shade of red can be obtained from various coal-tar derivatives. The method of working will modify the shade to a very great extent, in spite of the fact that the constitution of the resulting colour will be practically unaltered. Hence, an accurate knowledge of the working details of lake manufacturing is indispensable to the manufacturer of this series of bodies, as the processes are not merely those of "mixing".

The principal colouring matters which are employed for

the preparation of the red lakes are members of the following groups :—

1. The rosaniline group, or derivatives of triphenyl-methane, CH $(C_6H_5)_3$.

2. The rhodamine group, or derivatives of amido-phenol-phthaleins.

3. Azines, including the safranines, and the eurhodines.

4. The sulphonated azo compounds, typified by crocein scarlet.

5. The eosins, or halogen substituted phenol-phthaleins.

6. The alizarin group.

1. *The Rosaniline Group.*—The principal member of this group of colours, magenta, is that which is chiefly employed in the manufacture of lakes. Commercial magenta is in reality a mixture of the two colours, rosaniline and pararosaniline. The two bodies are, however, so nearly identical that with the exception of briefly indicating the difference in their constitution there is no need to further differentiate between them.

The parent substance of the group is the hydrocarbon triphenyl-methane, CH $(C_6H_5)_3$; the basic properties of the colours derived from this hydrocarbon being derived from amido groups introduced into the phenyl radical. Rosaniline is the triamido derivative of triphenyl-carbinol, of the constitution $C(OH)(C_6H_4NH_2)_3$, and differs only from pararosaniline in the fact that the latter is the corresponding derivative of tolyl-diphenyl-carbinol, of the constitution $C(OH)(C_6H_3 . CH_3 . NH_2)(C_6H_4NH_2)_2$. The colour (consisting of a mixture of the two bodies) is manufactured by the oxidation of ordinary aniline by either arsenic acid, mercuric nitrate, or nitrobenzene. The bases are, when pure, quite colourless, but they form salts (with the elimination of water) with acids, which are the real colours employed.

The usual form in which magenta is seen in commerce is

as the hydrochloride, the rosaniline salt having the composition $C_{20}H_{19}N_3HCl$, water being eliminated in the formation of the salt. It is then in the form of rhombic crystals which have a metallic green colour in reflected light. The solutions are crimson, and are not fluorescent. It is not very soluble in pure water, but is readily so in acidified water and in alcohol. Caustic alkalies separate the colourless base in the free state. Reducing agents, such as sulphurous acid, or zinc and acetic acid, decolourise solutions of magenta, eliminating the oxygen atom, with the formation of salts of leucaniline. After reduction in this way the solution is not re-oxidised by the action of the air (this distinguishes this colour from the somewhat similar colours, Magdala red and the safranines). Chloride of lime decolourises solutions of magenta.

Sometimes the acetate is found in commerce. It has the advantage of being the most soluble of the rosaniline salts. Magenta is a colour which should, when pure, consist only of the two colouring matters mentioned. Impurities modify the shade, and this is reproduced in the lake which is prepared from it. It is sold under numerous names, amongst which are the following : Magenta, azaleine, roseine, fuchsine, rubine, etc. Magenta-violet is a frequently occurring colour, and consists of a mixture of magenta and mauvaniline ; the lakes prepared from this colour are of a much more violet shade than those from the pure colour. Cerise is an impure magenta salted out from the mother liquors after the preparation of the pure magenta. It contains a certain amount of a colouring matter called phosphine. Cardinal and amaranth are also mixtures of magenta and various impurities.

Isorubin, or "new magenta," as it is called, is the corresponding hydrochloride of triamido-tritolylcarbinol, $C(OH)(C_6H_3.CH_3.NH_2)_3$. It is a colour of recent introduction, formed by the condensation of formaldehyde and

orthotoluidine. It resembles ordinary magenta in appearance and properties, but gives colours of a bluer shade, and is more soluble in water.

Maroon and grenadin are also more or less impure magenta.

Many of the lakes in which magenta is the chief ingredient are compound lakes manufactured from magenta mixed with one or more other colours, such as various scarlets or cherry reds. Amongst the best lakes of magenta are those prepared with arsenious or resinic acid (the latter being a mixture of various resin acids). The colour of these lakes is very bright, but the arsenious acid compound is somewhat fugitive. The tannic acid lakes are also fugitive, and somewhat dull. A lake prepared with antimony salts and tannic acid is very permanent, but not as bright as the arsenious acid lake. The tannic acid lakes have the property of being soluble in alcohol.

Magenta lakes, when undiluted, leave no ash, as they consist of organic bases in combination with volatile acids. Any ash present should be examined, and may be regarded as a diluent either added to lighten the shade, or as an adulterant for the purpose of cheapening the colour.

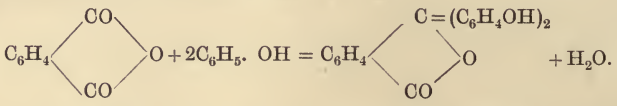
The colour should be entirely removed by treatment with sulphurous acid or by chloride of lime. In the former case exposure to the air does not restore the colour as it will do in the case of Magdala red and the safranines. If the lake be treated with a strong solution of caustic alkali, the free base may be dissolved out by ether. The colourless ethereal solution will dye silk a fine crimson, combination taking place between the base and some constituent of the fibre: or it will yield a fine crimson colour with a trace of acetic acid.

For a full recognition of the constituents of a compound lake prepared from several coal-tar colours, special works on

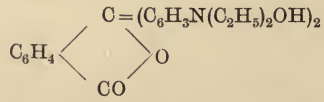
the analysis of this group of colours must be consulted. The enormous number of them, however, many of which are of almost identical properties, renders the task a matter of practical impossibility, unless the mixture is one of comparative simplicity.

A colour known as acid magenta, magenta S, or rubine S, is sometimes employed for lake manufacture. It is a trisulphonic acid of magenta, and forms lakes with bases instead of acids. Its colouring power is not so good as the basic colour, but it is very useful in combining with certain yellows for mixed shades. It is known also as acid fuchsine, and in an impure form as maroon S, grenat S, acid cerise, cardinal S, acid maroon, etc.

2. *The Rhodamine Group.*—When phenols are heated with phthalic anhydride, a combination takes place according to the following reaction :—



The resulting series of compounds are the phthaleins, which will be further referred to under the eosins. If amido derivatives of the phenols are treated in the same manner, amido-phthaleins result, which constitute the series of colours known as the rhodamines. Of these the body known simply as rhodamine is the type. This is prepared by the action of phthalic anhydride on diethyl-amidophenol. The resulting compound, which possesses simultaneously acid and basic properties, has the constitution



Here, as in the case of magenta, water is eliminated in salt formation, the commercial product being the hydro-

chloride, of the formula $C_{28}H_{30}N_2O_3$, HCl. The simplest possible rhodamine, of course, would be that obtained by the action of amidophenol on phthalic anhydride, but by the introduction of alkyl residues into the amidophenol the colour of the resulting body is much intensified, so that the compound above described is the body usually known under the name, which is in reality generic.

The amidophenol employed in the preparation of the rhodamines is the *meta* variety.

Commercial rhodamine forms a red powder, readily soluble in water, with a fine crimson colour and a characteristic yellow fluorescence, which is best observed in dilute solutions. By heating the solution to about 90° this disappears, and returns when the solution has cooled.

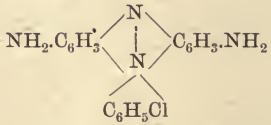
The free base is precipitated by the addition of caustic alkalies, in red flakes, soluble in ether. With stannous chloride, rhodamine gives a brilliant scarlet precipitate, which in a fine state of division shows a remarkable blue colour, somewhat resembling a fluorescence phenomenon. In strong sulphuric acid rhodamine dissolves with a yellow colour, which changes back to red on dilution with water. Rhodamine colours are very permanent to light.

In addition to the normal hydrochloride, the basic hydrochloride is well known under the name of rhodamine B. Numerous rhodamines are known, being the corresponding compounds of other alkyl-meta-amido-phenols.

Besides the ordinary rhodamine, the chief of those which are used for the production of lakes are the following: rhodamine B, the basic hydrochloride of diethyl-*m*-amidophenol-phthalein; rhodamine S, the succinein (in which succinic anhydride replaces phthalic anhydride) of dimethylamidophenol; rhodamine 6 G, the ethyl ester of diethylrhodamine; and rhodamine 12 G, a still further alkylised rhodamine.

In preparing the lakes of this group of colours, the best results are obtained by the use of tannic acid and tartar emetic, as the antimony and tannic acid lake is by far the least fugitive of the series, and none of them can be regarded as in any way permanent. These lakes are used to a certain extent for tinting violet lakes. When used for this purpose they are usually precipitated by a salt of phosphoric acid. The usual diluent of this lake is a fine variety of barium sulphate.

3. *The Azines.* (*a*) *Safranines.*—These compounds have a very complex constitution, all agreeing in containing two nitrogen atoms united to each other. The lowest member of the group is phenosafranine, the chloride of which probably has the constitution



The bases themselves are very little known, the salts of these being the colouring matters. As a rule they dissolve in strong sulphuric acid, with a fine green colour. On adding water the colour gradually changes to a bluish green, then to a distinct green. On further dilution violet and red shades appear.

By reduction with a reagent such as tin and hydrochloric acid, the colour is discharged, but it returns again on exposure to the air, thus differing from the rosaniline colours.

Alcohol dissolves the colour, forming a red solution with a yellow fluorescence. Dilute hydrochloric acid is without action, whilst concentrated acid changes the colour to a blue-violet. Ammonia and alkalies remove the colour, but without much alteration.

Commercial safranine consists of a mixture of several compounds, of which the best defined are the homologues, $C_{19}H_{17}N_4Cl$, $C_{20}H_{19}N_4Cl$ and $C_{21}H_{21}N_4Cl$. It is prepared in

various ways, and according to shade is known as : safranine, safranine T, aniline pink, safranine extra G, safranine S, safranine GGS, safranine GOOO, safranine FF, safranine AG and AGT extra.

Dimethyl-phenosafranine is the base of the colour known as fuchsia. Magdala red is a colour which is best classed with the safranines, if it does not actually belong to that class. It is a very useful colour, known also as naphthalene red, napthalene rose, naphthalene scarlet, Sudan red and rose pink. It has the formula $C_{30}H_{21}N_4Cl + H_2O$. It occurs in commerce as a hydrochloride. It is very slightly soluble in water, and is characterised by its cherry-red colour in alcohol, with a cinnabar-coloured fluorescence. The solution loses its fluorescence by the addition of ammonia. It is distinguished from eosin by not being dissolved from its compounds by alcohol, and by not being easily decomposed by strong alkalies or dilute acids.

Reducing agents decolourise the solutions, the colour returning on exposure to the air.

The only satisfactory lakes of the safranine group are those prepared with tartar emetic and tannic acid. They are much brighter than the corresponding magenta lakes, and are also much faster.

(*b*) *The Eurhodines.*—This group of colours might almost be classed with the safranines, as they differ from them only in that they are azines in which one atom of hydrogen has been replaced by an amido group, whereas in the safranines two atoms have been so replaced. The separation of the eurodines into a separate class is due to Otto Witt, whose classification we follow in this respect. The chief colour in this group, which is used for the production of lakes, is that known as toluylene red, or neutral red. This compound is the hydrochloride of the base dimethyl-diamidotoluphenazine, of the formula $C_{15}H_{16}N_4 \cdot HCl$, and occurs as a greenish-black powder,

easily soluble in water, which turns bluer and finally loses its colour on heating with reducing agents. The colour, however, returns on exposure to the air. It gives a fine red solution in alcohol, with a brownish fluorescence. With hydrochloric acid its solution becomes blue. It forms a good lake with tannic acid and tartar emetic, which has a blue-red tone. The closely allied neutral violet, of the formula $C_{14}H_{14}N_4HCl$, is a homologue of the above colour, being the hydrochloride of dimethyl-diamidophenazine. It is a violet colour, but the tannic acid and tartar emetic lake is of a fine red-violet tint.

4. *The Sulphonated Azo-compounds.*—The sulpho acids of the azo colours are amongst the most important of all the coal-tar colours, not only for lake production, but also for all purposes for which the colours are used. They are so numerous, their number having increased to such an extent of recent years, that it is impossible to do more than give short details of the principal of those which are used for the production of the more important of the red lakes.

It is necessary, in order to get a clear idea of the substances with which we now have to deal, to understand the principles involved in the preparation of the several groups comprising the azo colours. The fact that they may now be regarded as the most important series of the coal-tar colouring matters, and have in themselves given a fresh impetus to an already important industry, justifies a somewhat fuller treatment than might at first appear necessary in a technical work of the character of the present volume.

(4) *Azo Compounds.*—The azo dyes form a well-defined and well-understood group of compounds. They are prepared by the action of diazo compounds on phenols or amines of the aromatic series. The diazo compounds themselves result when salts of primary amines of the aromatic series are treated with nitrous acid. The typical reaction illustrating this important change is that of nitrous acid on aniline, as follows:—

$$\underset{\text{Aniline hydrochloride}}{C_6H_5.NH_2.HCl} + \underset{\text{Nitrous acid}}{HNO_2} = \underset{\text{Diazobenzene chloride}}{C_6H_5.N:N.Cl} + \underset{\text{Water}}{2H_2O}$$

If aniline in alcoholic solution be treated with nitrous acid, the resulting product is diazoamidobenzene. This body may be regarded as due to the previous formation of free diazobenzene, which then reacts with another molecule of aniline, thus :—

$$C_6H_5N:N.OH + C_6H_5NH_2 = \underset{\text{Diazoamidobenzene}}{C_6H_5N:N.NH.C_6H_5} + H_2O.$$

The diazo compounds are thus characterised by containing the group N : N, which is combined with one carbon atom and with one atom other than carbon.

The azo compounds, on the other hand, contain this same important group, N : N, but it is combined with two carbon atoms, this constituting the difference between the two series of bodies. The simplest type of the azo compounds is ordinary azobenzene $C_6H_5N:NC_6H_5$.

Azobenzene and its homologues can be obtained by the reduction of the nitro derivatives of the corresponding hydrocarbons. The most suitable reducing agents are sodium amalgam, or zinc and alcoholic potash. The typical reaction takes place as follows :—

$$2C_6H_5NO_2 + 4H_2 = C_6H_5N:NC_6H_5 + 4H_2O.$$

The simple azo compounds are usually highly coloured bodies, but they are not colouring matters, as they possess no power of combining with either acids or bases. The real colour bodies employed are amido or hydroxy derivatives of the azo compounds. The types of these two series are :—

$C_6H_5N:NC_6H_4.NH_2$	Amidoazobenzene
$C_6H_5N:NC_6H_4.OH$	Hydroxyazobenzene

The amidoazo compounds can be employed as such when they possess basic properties, combining with acids, and they can also be used in the form of their sulpho acids, when they

are of an acid character. The preparation of benzene azo β naphthylamine will serve as an example of the usual method of preparing amidoazo compounds. One molecule of β naphthylamine is dissolved in dilute hydrochloric acid by the aid of heat, filtered from any impurity insoluble in acid, very considerably diluted and cooled. One molecule of aniline hydrochloride is dissolved in water, and a considerable excess of hydrochloric acid added to prevent formation of diazoamidobenzene on diazotisation, and one molecule of sodium nitrite added slowly to the cooled liquid. This solution of diazobenzene hydrochloride is filtered into the β naphthylamine solution with constant stirring, and the mixture allowed to stand for several hours to allow combination to take place, when a red precipitate of benzene azo β naphthylamine separates in accordance with the following scheme :—

$$C_6H_5N_2Cl + C_{10}H_7NH_2 = C_6H_5N_2C_{10}H_6NH_2 + HCl.$$

Substituting other amines or their sulpho acids for the aniline and other amines, or phenols or their sulpho acids for the naphthylamine, we may prepare other azo compounds. The hydroxyazo compounds are almost invariably used as sulpho acids, and this series of colours is perhaps the chief of all those used in the manufacture of coal-tar lakes. Amongst the amidoazo colours themselves only one is used to any extent for assisting in the production of red lakes. This is the well-known dye chrysoidine, a more or less orange colour, but which is used to give certain shades to other well-defined red lakes. Chrysoidine is the hydrochloride of diamidoazobenzene, $C_6H_5N:NC_6H_3(NH_2)_2HCl$. Being a strongly basic colour it can be used to advantage with magenta, and in this combination it is known under the name of cardinal, a name applied, however, to several other colours. A scarlet is also sold which is a mixture of

safranine and chrysoidine. The lakes of these colours are usually prepared as described under magenta and safranine.

The oxyazo colours may be said to be now the most important of all the coal-tar colours, and owe their existence to the researches of the late Peter Greiss, who published his investigations on these colours in 1878. Since that time the chemistry of this group has advanced to an enormous extent, and new colours are constantly being discovered. As a general rule these colours are superior to the other earlier known compounds, both in brilliancy and in permanence.

In the following short description of the more important of the sulphonated azo colours, it must be remembered that in actual practice the colours are not usually the pure compounds here mentioned, but are composed of a mixture of closely similar compounds. The usual initials used to designate the intensity of the shade (depending on the exact degree of alkylisation, etc., of the parent compound) are added where necessary; these are R (= roth, red) and G (= gelb, yellow).

The following are the constitutions and technical names of the principal colours :—

Crocein.—The enormous number of varieties of this splendid colour, all of which may be employed according to the shade desired, are all closely related compounds. Typical amongst them is that known as Crocein 3BX. This is the diazo combination of naphthionic acid combined with one of the many β naphthol-sulphonic acids. Chemically, its name is sodium naphthalene-sulphonate-azo β naphthol α sulphonate of sodium. In addition to this compound the following croceins are well defined, all being similar compounds in which the benzene, toluene and naphthalene groups replace one another in various ways. Crocein scarlet 3R (= scarlet 4RB), crocein scarlet 7B (= scarlet 6RB) and brilliant crocein, are all diazo compounds of closely related

bodies in combination with one of the naphthol-sulphonic acids.

Biebrich scarlet is one of the most useful compounds. It is a combination of the diazo compound of amidoazobenzene-disulphonic acid and β-naphthol. Xylidene red is also much employed. This is the compound of the diazo derivative of xylidene and one of the naphthol-disulphonic acids.

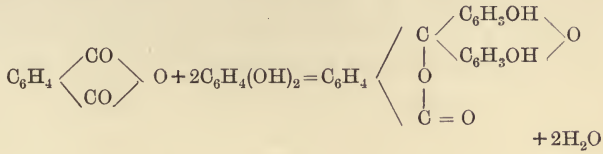
The xylidene scarlets are such brilliant and permanent colours that they are, to a considerable extent, displacing the natural cochineal carmine.

In preparing the lakes of these hydroxy-sulphonic-azo compounds, the best base for general use is alumina. The shades produced by the use of this base are more brilliant and clear than those made in any other manner. Most of the metallic salts yield precipitates with these colours, but they are, as a rule, soluble to a certain extent in large excess of water; therefore in their preparation a loss of colour is often experienced. As a rule, the colour is largely diluted with an inert material, such as sulphate of barium; in the preparation of the diluted colour, it is best to precipitate the lake and the barium sulphate from a solution of alum and barium chloride simultaneously, as the colour is then intimately incorporated with the diluent. As a rule, the lakes from this group of colours, as is the case with many others, have a somewhat bluish shade when prepared from a single compound. It is therefore usual to use a mixture of colours in which there is sufficient orange to entirely overcome the blue shade.

Although, as a class, these colours are fairly fast to light, it has been observed that their permanence usually increases with increase in molecular weight.

5. *The Eosins.*—As has been mentioned earlier, phthalic anhydride and the phenols possess the power of combination, with the formation of a group of bodies known as the

phthaleins. If, instead of using the monatomic phenols, one employs the dihydroxy phenol, resorcinol (meta-dihydroxy-benzene), a phthalein of great interest is obtained. The reaction taking place is as follows :—



The resulting compound is fluorescein, a yellowish-red powder, which even in the most dilute solution shows an intense greenish fluorescence. So intense is its colouring power, that whole rivers may be coloured for miles by a single pound or so of it. It has indeed been used to trace the course of underground streams, and the existence of an underground connection between the Danube and the Ach, a small river running into the Lake of Constance, has been proved by its use.

The eosins are derivatives of fluorescein, in which a certain number of the hydrogen atoms are replaced by halogen atoms, that is by chlorine, bromine or iodine, the last-named being very expensive; the usual commercial eosins are bromine compounds. The iodine compounds are generally termed Erythrosins. The most important of these bodies are the following :—

Eosin (Eosin yellowish, Soluble Eosin, Eosin A, etc.) is tetrabrom-fluorescein $C_{20}H_8Br_4O_5$. It comes into commerce as its potassium salt, $C_{20}H_6Br_4O_5K_2 + 6H_2O$. It is then marked (in German commerce) Eosin J. It is a reddish powder with a yellowish-green reflex. Its solutions are intensely rose-coloured, with a very fine green fluorescence. Its acid properties are very marked, its salts not being decomposed by acetic acid. It combines with metallic

oxides, forming very insoluble lakes. Silver and lead salts give red, aluminium and tin give red-yellow lakes.

Eosin orange, or Eosin 5 G, is a mixture of the tetrabromo with the dibromo compound.

Erythrosin (Eosin blue shade, Pyrosin R, Dianthin B, etc.) is tetraiodo-fluorescein. It closely resembles ordinary eosin, but its solutions are not fluorescent.

Aureosin is a mixture of chlorinated fluoresceins.

Various bromnitro-fluoresceins are known in commerce; they are called safrosin or Eosin BN. A mixture of bromnitro- and of nitro-fluoresceins is also known as Lutecienne. A nitrochlor-fluorescein is sold as Rubeosin.

Various methyl and ethyl derivatives of the eosins are also occasionally met with. They are called spirit-soluble eosins, and are sold under such names as Eosin BB, spirit primrose, Rose JB (soluble in spirit).

Rose Bengale, a favourite colour, is the sodium salt of tetraiodo-dichlor-fluorescein.

Phloxin (Phloxin TA) is the potassium salt of tetrabrom-tetrachlor-fluorescein.

Cyanosin is the potassium salt of the methyl ether of tetrabrom-dichlor-fluorescein.

These colours readily yield lakes with salts of lead, aluminium, zinc, tin, etc., of great colouring and covering power, but they are very fugitive.

Lead salts give the bluest shades, whilst tin and aluminium lakes are of a much more yellow tint. The usual inert matter used as a diluent is barium sulphate, but sometimes eosin lakes are met with containing nothing but lead salts, both as the precipitant for the lake and as the inert base.

The now very common "vermilionettes" are eosine lakes with a lead base, mixed either with lead sulphate or with barium sulphate. We have frequently met with vermilion, sold as pure, containing up to 50 per cent. of sulphate of lead

with a small quantity of a lead-eosin lake. The fugitive nature of this colour renders such an adulteration very pernicious.

Alizarin Compounds.

All that is necessary in connection with the alizarin lakes for the present purpose has been said under madder lakes, to which section the reader is referred. The close relationship of the colouring matters of madder to the artificial colours renders it more convenient to deal with the two sets of colours together.

Orange and Yellow Lakes.

The lakes of these colours need only be referred to shortly, as the main principles of the chemistry of the groups of colours to which they belong have been dealt with at sufficiently full length in describing the red lakes. Nearly all the orange colours employed for the preparation of lakes are sulphonic acids of the azo colours, closely related to the azo reds. Types of these are the following :—

Mandarin (Orange II, Tropœolin OOO No. 2) is benzene-sulphonate of sodium-azo-β-naphthol.

Mandarin GR (Orange T, Orange R) is different from this only in the fact that the benzene is replaced by orthotoluene.

In all respects the principles governing the formation of red lakes of this class apply to the orange lakes. An imitation red lead is often met with, consisting of a lead lake of a cheap orange, precipitated together with a large amount of barium sulphate. The orange lakes are not very permanent. Yellow lakes are not of very frequent occurrence, as the use of chrome yellows is very satisfactory, and their production is much cheaper than that of the yellow lakes. They are, however, used to a certain extent to modify the shades of green lakes. The principal colours used are the following :—

The basic colour auramine (imido-tetramethyl-diparadiamidodiphenylmethane). It gives an excellent lake with tannic acid and tartar emetic.

Thioflavine (dehydro-thiotoluidine trimethyl-chloride). This also gives good results with tannic acid.

Amongst the acid yellows used for lakes are the following: Tartrazine: this is the trisodium salt of tartrazinic acid. Naphthol yellow. Quinoline yellow and metanil yellow. These are often used as simple barium lakes, with barium sulphate as a diluent. The colours are, however, very fugitive, and better results are obtained when metanil yellow, which possesses acid and to a certain extent basic properties, is used in the form of a tannic acid and barium lake.

Green and Blue Lakes.

The majority of the green lakes usually met with are made from basic colours of the triphenylmethane group (see rosaniline), or from sulpho-acids of basic colours, in which both the acid and the amido groups have been neutralised in the formation of the lake. A certain number are also made from purely acid greens, such as certain sulpho-acids of azine or azo-greens, and some alizarin derivatives.

Methyl green is the most important of the basic greens from many points of view. It is the zinc chloride compound of the hydrochloride of chlor-methyl-hexamethyl-pararosaniline, of the formula $C_{19}H_{12}(CH_3)_6N_3.Cl.CH_3Cl + ZnCl_2 + H_2O$. It is readily soluble in water and alcohol, and also in amyl alcohol. This last character distinguishes it from benzaldehyde green and its allies. By heat it splits up into methyl chloride and methyl violet. Hence, by moistening a filter paper with a solution of this colour and strongly drying it, the colour turns to a fine violet. Strong hydrochloric acid

turns the colour yellow, and alkalies and reducing agents decolourise the pigment.

Iodine green closely resembles the last described compound. It was in former times manufactured by using methyl iodide instead of methyl chloride, but the iodine compound is seldom met with now, and much of the so-called iodine green contains no iodine at all.

Malachite green (Victoria green, Benzaldehyde green) is usually met with as the oxalate or the zinc chloride double salt. The free base is tetramethyldiamidotriphenylcarbinol, of the formula $C(OH)\ (C_6H_5)\ (C_6H_4N.\ (CH_3)_2)_2$. As is usual with this group of colours, water is lost in the process of salt formation, and the oxalate has the composition $2C_{23}H_{24}N_2 + 3C_2H_2O_4$.

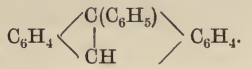
Ethyl green is the corresponding ethyl compound.

Acid green, SOF, is the sodium salt of diethyldibenzyldiamidotriphenylcarbinol trisulphonic acid. This body is also known as diamond green and dragon green.

When the purely basic greens are used the acid used for precipitation is arsenious acid, which gives by far the most brilliant shade possible. The tannic acid and tartar emetic lakes are dull, but at the same time useful for certain purposes.

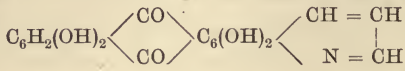
When such colours as diamond green are used, barium chloride is a favourite precipitant, but the amido groups in the colour should first be saturated with tannic acid or some other acid. Sometimes an acid yellow is employed with the acid greens to tint the resulting lake, and if picric acid be used it also serves the purpose of saturating the amido groups present.

Cœrulein is a green colour made by heating gallein (the phthalic anhydride compound of pyrogallol) with sulphuric acid. Its constitution is not certain, but it is probably an anthracene derivative of the formula—



It gives very fast, but somewhat dull shades with most metallic salts. With chromium salts it gives a splendid dull olive green which is as fast to light as any of the alizarin greens.

There are several varieties of alizarin green, of very complicated constitution. The principal of these is alizarin green G, the parent substance of which has the constitution



The actual dye is a mixture of sulpho-acids of this body and of *tri-* and *penta*-oxyanthraquinone quinoline. Various shades are produced according to the degree to which the sulphonation has gone, and also according to the number of OH groups introduced. The others are closely related to this body, and their lakes are formed in the same manner as the alizarin reds, which have been described under the madder lakes

There are not a great many blue lakes manufactured, as they are, in general, rather fugitive, and the ultramarine and Prussian blue colours are so permanent and cheap that they are usually preferred to the coal-tar colour lakes.

The colours, however, from which blue lakes are made (and also violet lakes, which are generally very closely related to the blue colours) belong to the following series : (1) The triphenyl-methane compounds ; (2) the sulpho acids of those compounds ; (3) the azines ; (4) the indulines. A few other compounds are occasionally employed.

If the hydrogen atoms of the amido groups of rosaniline or pararosaniline be replaced by organic radicles the colour becomes violet or blue. The shade is bluer according as there are more hydrogen atoms so replaced. The ethyl de-

rivatives are of a redder shade, the methyl and benzyl derivatives less red, and the phenyl derivatives of the finest pure blue colour. Of the purely basic blues and violets, the substituted magentas are perhaps amongst the best known.

Aniline blue (spirit soluble blue, gentian blue, opal blue) is triphenyl-rosaniline, of the formula $C_{20}H_{16}(C_6H_5)_3N_3$. The commercial blue is a mixture of compounds of various degrees of alkylisation, the more highly alkylised being of the bluest shades ; it is sold in the form of its hydrochloride.

Spirit soluble diphenylamine blue, $C_{19}H_{14}(C_6H_5)_3N$, is identical with the last described compound in chemical composition, except that it is triphenylated *para*-rosaniline. It is not practicable to introduce more than three phenyl groups into this series of compounds, but more ethyl and methyl groups may be added, the resulting blues being very intense. Both series of compounds may be sulphonated, and the resulting so-called "soluble" blues are the most generally useful for lake production. In addition to the bodies included in the above series, the azine group is represented by Nile blue, naphthylene blue and methylene blue ; and the indulines by "neutral blue". These will be found referred to in the table at the end of the chapter.

Tartrate of antimony and tannic acid are generally used as the precipitants of these blue colours. If hydroxy groups are present in the colour base, they should be neutralised by the addition of barium hydroxide. Sometimes zinc and aluminum salts are used to a small extent.

Violet lakes in general are treated in the same manner as blue lakes, but it is to be noted that the most brilliant lakes are yielded by the basic violet colours precipitated by means of phosphoric acid.

Gallein, the phthalein of pyrogallic acid, of the formula $C_{20}H_{10}O_7$, is largely employed for the manufacture of violet lakes, with potassium bichromate and tartar emetic. It

yields lakes with a fine "bloom". With lead acetate it gives a fine grey-violet lake. The black lakes, which are in reality an intensely blue black, are prepared from certain acid azo colours. They are, however, usually mixed with certain blacks to modify the shade, and are seldom employed by themselves.

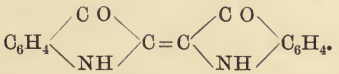
INDIGO.

The importance of this colour as a dyeing material cannot be overestimated, but as a pigment, although it finds a certain employment, it is equalled in permanence, without losing at all in richness of colour, by some of the cheaper blue pigments. Hence, and on account of its high price, it is only employed to a limited extent for certain fine work. Indigo was until quite recently the product only of certain plants; the artificial preparation of the colour, however, was achieved some time ago, Prof. Baeyer, of Munich, taking out a patent in 1880 for "the preparation of derivatives and homologues of ortho-nitro-cinnamic acid, and their conversion into indigo blue and allied dye stuffs". This triumph in chemical science was met with little more than amusement by the indigo planters and traders, but within the last few years synthetic indigo—rather dearer, but purer than the natural colour—has become a commercial article, and it is certain that before very long its price will be reduced as easier processes are discovered, as they are sure to be. In spite of this the indigo planters go on in the same way that they have always done, without, except in rare cases, any attempt at improvement in their methods. This has called forth a very emphatic warning from Prof. Armstrong, and there is little doubt that, unless every help that science can afford is rapidly brought to bear on the natural production of indigo, the experience of the madder industry will be repeated, in which the production of synthetic alizarin in

time killed the natural madder production, and threw open large tracts of cultivated land for the cultivation of other crops.

The principal members of the leguminous genus, *Indigofera*, producing indigo, are *I. tinctoria* (the most important), and *I. disperma*, *anil* and *argentea*. Indigo does not exist as such in the plants, but is produced by the action of a ferment on a glucoside contained in them, called indican, which may be extracted from them by means of cold alcohol.

Indigotin, or indigo blue, as it is often termed, was formerly described as of the formula C_8H_5NO, but is now well established as of the formula $C_{16}H_{10}N_2O_2$ and the constitution



Pure indigotin may be obtained from commercial indigo, which contains from 20 to 90 per cent. of it, by mixing it with plaster of Paris and water, spreading the mass on an iron plate, and heating it cautiously to sublime the indigotin, which may be removed from the surface by a fine spatula. It is prepared by the oxidation of indigo-white (see below), in a state of fair purity, but to obtain the finest specimens of the colour the aid of synthetic methods must be invoked.

Pure indigotin forms fine deep blue crystals with a coppery sheen, subliming at about 290° C. It is insoluble in water, cold alcohol, ether, and in essential oils, but soluble in acetic acid, aniline, and nitrobenzene. It may be purified by boiling it with aniline to saturation, filtering and allowing the crystals to be deposited, and then washing them with alcohol. It is a neutral body, and is not affected by dilute acids or alkalies. As a dye it is largely employed for cloth, but in the form of a pigment it has but a limited use, either

as an intense deep blue, or as a mixed colour with yellows, or as a light blue diluted with a white.

Indigo-white is hydindigotin, or reduced indigo, of the formula $C_{16}H_{12}N_2O_2$. It is obtained by reducing indigotin with any of the usual reducing agents. It is of interest only to the dyeing industry, on account of the fact that it dissolves easily in alkalies, and the weak compound thus formed, when absorbed by the fibre, is decomposed by the latter, and the indigo-white is fixed by some unknown constituent. On exposure to weak oxidising agents (such as the atmosphere), the indigo-white is re-oxidised to indigotin, and the fibres assume the well-known blue colour.

Commercial indigo, made from the plants, consists chiefly of the body indigotin (see below). To obtain the indigo, the plants are chopped—or rather those parts in which the colour compounds are found, *viz.*, the leaves and twigs—and immersed in water. After a certain time fermentation has gone on to the proper degree, and the water is run off into shallow vats, and is well agitated in order to expose it as much as possible to the action of the air. The yellow liquid assumes a greenish colour, and the indigo separates in a pulpy state. The blue pulp is boiled with water in order to prevent secondary fermentation setting in, which would result in the formation of brown products. After a certain time the liquid is filtered and the precipitate pressed, and slowly dried in sheds from which the light is excluded as far as possible.

The indigo thus obtained varies very greatly in quality, both as far as its content in true indigotin and in the amount of mineral impurity it contains. Apart from the plants of the *Indigoferæ*, several other species yield the colour, among which the best known is the woad plant, *Isatis tinctoria*, and several kinds of orchids also contain it in small quantities. The chemistry of the group of compounds belonging to the

indigotin series is too extensive a subject to be adequately dealt with in a work of this kind, and the reader is therefore referred to text-books on organic chemistry for fuller details than the short account which follows contains.

Indican, $C_{52}H_{62}N_2O_{34}$, is the glucoside from which the indigotin is derived. It forms a brown syrup, from which the last traces of water cannot be separated without great trouble, if indeed it is possible at all to remove them. The reaction by which the indigotin and glucose are formed is as follows :—

$$C_{52}H_{62}N_2O_{34} + 4H_2O = C_{16}H_{10}N_2O_2 + 6C_6H_{10}O_6.$$

On treatment with strong sulphuric acid, indigotin yields sulphonic acids. The bodies accompanying indigotin in commercial indigo also yield such acids, and the resulting mixture of sulpho acids is known as soluble indigo, or indigo carmine. The exact properties of indigo carmine vary according to the nature of the initial indigo and to the details of manufacture; with a moderate proportion of acid, the principal body formed is a mono-sulphonic acid, $C_{16}H_9N_2O_2,SO_3H$, which, as its sodium salt, is known as indigo-purple. With excess of acid, a di-sulphonic acid, $C_{16}H_8N_2O_2(SO_3H)_2$, known as sulphindigotic acid, is formed. The indigo carmine of commerce is the sodium salt of the sulphonated indigo.

A typical sample of commercial indigo analysed by Giradin was found to be composed as follows :—

Indigotin, $C_{16}H_{10}N_2O_2$	61·4
Indigo red, $C_{16}H_{10}N_2O_2$	7·2
Indigo brown	4·6
Indiglucin, $C_6H_{10}O_6$	1·5
Ash	19·6
Water	5·7

The preparation of synthetic indigo may be achieved in several methods. For the historical details of the synthesis Richter's *Organic Chemistry*, vol. ii., may be consulted. The

commercial synthetic indigo now on the market, which is claimed to contain 97 per cent. of pure indigotin, is prepared in the following manner: Naphthalene, $C_{10}H_8$, is oxidised to phthalic acid, $C_6H_4\begin{cases}COOH\\COOH\end{cases}$, and this is converted into phthalimide, $C_6H_4\begin{cases}CO\\CO\end{cases}NH$. This is then converted into anthranilic acid, $C_6H_4\begin{cases}COOH\\NH_2\end{cases}$, and then into phenylglycine-orthocarboxylic acid, $C_6H_4\begin{cases}COOH\\NH.\ CH.\ COOH\end{cases}$, and this into indoxylcarboxylic acid, $C_6H_4\begin{cases}CO\\NH\end{cases}CH.\ COOH$, which is finally converted into indigotin,

$$C_6H_4\begin{cases}CO\\NH\end{cases}C:C\begin{cases}CO\\NH\end{cases}C_6H_4.$$

In analysing indigo it is important to determine the amount of moisture and ash, and also the percentage of true colouring matter. It depends on circumstances whether it is necessary to determine the actual amount of indigotin separately from the total amount of colouring matter.

The moisture in good commercial indigo varies from about 3 to 9 per cent., and may be driven off in the usual manner by drying at 100° C.

In good samples the ash falls as low as 2 per cent., but in fair commercial samples of undoubted purity it may often reach from 5 to 8 per cent. Some of the inferior kinds, such as that from Madras, may contain as much as 25 per cent.

It has been proposed to determine the specific gravity of the sample, but in the authors' experience this is without any value in judging the quality of indigo.

Starch is said to be occasionally used as an adulterant of indigo, but the authors have never met with it in any sample they have examined. If it is thought necessary to look for

this body, the best plan is to boil the sample with water, and after cooling to test the filtered liquid with a solution of iodine, when the well-known blue colour will result.

According to A. H. Allen, a useful proximate analysis of indigo may be effected in the following manner. The sample is dried at 100° in order to determine the moisture, and the dry residue is treated with hot water, and the residue dried and weighed. This gives the amount of impurities soluble in water. The residue is then treated with hydrochloric acid and then with dilute alkali, the residues being weighed after each treatment in order to determine the amount dissolved by these solvents. It is then treated with alcohol, and the amount dissolved determined. This very fairly represents the amount of indigo red, which may be of importance to determine, as it modifies the blue shade of the indigo.

The residue, after allowing for the ash it leaves on ignition, very fairly represents the amount of indigotin.

C. T. Lee proposes to determine the amount of true indigotin by observing the amount which can be obtained by sublimation—a method which is easy to carry out, and which yields satisfactory results under certain conditions. A more accurate method of determining the amount of true indigotin is that based on the reduction of this body to indigo white and its subsequent reoxidation by exposure to the air. The process recommended by C. Rawson is as follows: One gramme of the finely powdered sample is treated in a flask with 2 grammes of crystallised ferrous sulphate and 5 gr. of caustic soda in 1000 c.c. of water. The flask is closed by a cork, which has three perforations, through one of which passes a syphon, whilst the other two are used respectively for the entrance and exit of a current of coal gas. The contents of the flask are maintained for about two hours at a temperature just below 100° C., and after removing the source of heat the insoluble matter is allowed to subside; 500 c.c.

(representing 0·5 gr. of the sample) of the liquid, which is made up to 1000 c.c. exactly, after cooling, with well boiled distilled water, unless it is preferred to make an allowance for the quantity of water lost during the heating of the liquid, is then syphoned off and the reduced indigo is oxidised by allowing a current of air to pass through the liquid. To complete the precipitation, the liquid is acidified and the precipitate of indigotin, together with the indigo-red and the indigo-brown, is allowed to subside. The supernatant liquid is passed through a tared filter, and the precipitate washed several times with hot water by decantation, and then boiled with alcohol to dissolve the red and brown colouring matter. The alcoholic liquid is then allowed to cool in order to ensure the deposition of any traces of dissolved indigotin, and the residue then collected on the filter and dried and weighed after washing with absolute alcohol.

There are many other methods for an accurate assay of indigo, but for the purpose of the present work it is unnecessary to deal further with the subject. For fuller details of the numerous processes, the reader is referred to Allen's *Commercial Organic Analysis*, vol. iii., part i., in which a very full account of the subject will be found.

VARIOUS UNCLASSIFIED PIGMENTS.

Dragon's Blood.

The ordinary dragon's blood of commerce, which is imported in the form of sticks or lumps, is a resinous product of the fruit of several different plants, of which the chief appears to be *Dæmonodrops Draco*. This product is known as palm dragon's blood, and is imported from Southern Asia. A very similar, but less esteemed product, is the Socotra dragon's blood obtained from the fruits of *Dracæna Cinnabari*. Other products are also used.

The crude resinous product is of a deep red colour, varying much in quality, and when powdered forms an intensely red powder, which is not used in medicine, but is largely employed for colouring varnishes and polishes. It forms the basis of the majority of the so-called mahogany stains. As a pigment it finds only a limited employment.

According to Dieterich, the resinous product consists of the following compounds: dracoalban, a white amorphous powder, softening at 192°, and probably of the composition $C_{20}H_{40}O_4$; this body occurs to the extent of about 2·5 per cent.; dracoresene, a bright yellow amorphous resin, melting at 74°, occurring to the extent of about 14 per cent.; red resin, the true colouring matter, about 55 to 60 per cent. This body consists mainly of the benzoate and the benzoyl-acetate of a complex alcohol, dracoresinotannol, C_8H_9O. OH. Of these esters the former largely preponderates.

There are in addition small quantities of other resinous bodies, and in most samples certain quantities of woody fibre and other vegetable matter, and about 8 per cent. of mineral matter.

The powdered resin is of a somewhat high value, and is therefore liable to considerable adulteration. The chief substances used for the purpose of sophistication are oxide of iron, powdered bole, common colophony, and finely powdered red Sanders wood. The grosser adulterations, such as iron oxide or powdered bole, etc., will be left as a residue when the resin is treated with solvents, such as alcohol and ether. The microscope will reveal the presence of any appreciable quantity of woody fibres, and the iron oxide will be found in the ash and can be estimated in the usual manner.

According to Hirschsohn, the saponification number (number of millegrams required to saponify one gram of the resin) is about 150.

Gamboge (*Gamboge*).

This pigment is a gum-resin yielded by several trees growing in various parts of the Malay Peninsula, and in Ceylon. It comes into commerce, as a rule, in the form of cylindrical rolls, which are prepared by running the exuded juice into hollow bamboo canes. When broken the mass of gamboge exhibits a conchoidal or vitreous fracture, and is of a fine yellow red colour. When powdered the colour is of a very fine yellow. The finest qualities of gamboge are very brittle, and are nearly odourless; it has little taste at first, but after a time it causes a sensation of acridity in the throat. By the successive action of ether and water it is almost entirely dissolved. When in the powdered form it is often adulterated, either with starch or with mineral matter. The former adulterant is best tested for by the usual reaction for starch. A decoction of the gamboge when cooled does not become green when a little solution of iodine is added to it, but merely of a tawny colour. Inferior varieties of the mass gum-resin often contain appreciable quantities of woody fibre, etc., and on grinding this is naturally found in the powder. The ash of pure gamboge is usually about 0·5 per cent., or even less, and should certainly not exceed 1 per cent. If it does the presence of added mineral matter may be inferred, and the ash should be carefully examined. A number of samples were examined by Christison many years ago (*Companion to the Botanical Magazine*, ii., 233), and he gives the following results :—

	Siam Gamboge.			Ceylon Gamboge.
	Pipe.	Lump.	Coarse.	
Resin	71·6—74·2	64·3—65·0	35 —61·4	68·8—72·9
Soluble gum	21·8—24·0	19·7—20·7	14·2—17·2	18·8—20·7
Woody fibre	Traces	4·4— 6·2	7·8—19·0	4·3— 6·8
Starchy matter	—	5·0— 6·2	7·8—22·0	—
Moisture	4·8	4·0— 4·2	7·2—10·6	Not determined

Those samples containing starch are obviously adulterated.

A solution of gamboge is acid in reaction, owing to the presence of a peculiar resin acid called cambogic acid. The approximate composition of normal gamboge may be regarded as follows: Moisture, from 1 to 4 per cent.; resins, chiefly of an acid nature, 65 to 70 per cent.; gum, from 15 to 25 per cent.; wax, under 5 per cent.; mineral matter, under 1 per cent. The gum resin contains no essential oil. Although starch and mineral matter may be regarded as the most usual adulterants, samples have been found mixed with common resin and with dextrin.

The quantitative action of caustic alkalies on gamboge is a useful criterion of its purity. Several chemists have examined the gum-resin from this point of view. According to Williams the acid number (number of millegrams of caustic potash, KOH, used to neutralise the free acids) of a genuine sample was 80·6; the ester number 67·2, and the total saponification number 147·8. Kremel gives 100·0 for the acid, and 56·7 for the ester numbers. Beckurts and Brüche give for four samples the following figures: Acid numbers, 89, 81, 69 and 71; for the ester numbers, 61, 50, 43 and 44.

Gamboge is partly soluble in alcohol, ether and ammonia. The ammoniacal solution gives a red precipitate with barium salts, yellow with zinc salts, red-yellow with lead salts, and brownish-yellow with silver salts.

Buchner has examined the resin acids of gamboge, and although the chemistry of these bodies is but poorly understood, there is good evidence that the formula for the chief of these acids, which is termed cambogic or gambogic acid, is $C_{30}H_{35}O_6$.

Gamboge is, in painting work, chiefly employed as a water colour, as a bright yellow, or in admixture with blues, to form dull greens. It is very useful as a glazing colour, but is not permanent in sunlight.

Sepia.

This dark brown ink-like pigment is contained in the ink bag, a defensive weapon, of the ordinary cuttle fish, *Sepia officinalis*, of *Sepia loligo*, and other cephalopods, the "shells" of which are often thrown up on our sea-beaches.

The ink obtained from this source, and which the animal has the power of ejecting at will, in order either to effect its escape in the clouded water, or for offensive purposes, was known to the ancients. Horace in his Fourth Satire speaks of *nigræ succus loliginis*. Aristotle also mentions the sepia, but rather as a table delicacy than as a pigment bearer.

The juice, or ink, should be taken from the animal soon after capture, as it is liable to putrefaction, and when dried forms a black mass which, according to Prout, whose analysis is the only one we have seen, consists of

Black pigment (melanin)	78·00
Calcium carbonate	10·40
Magnesium carbonate	7·00
Alkaline sulphates and chlorides	2·16
Mucus	0·84
	98·40

The black pigment is isolated by boiling the dried mass with water, hydrochloric acid and ammonium carbonate successively. These menstrua presumably remove the mineral matter and mucus, and leave the colour as an insoluble residue.

Sepia is insoluble in water, alcohol and ether, but remains suspended in water for a time, hence its use as an ink. Its deposition is accelerated by acids or ammonium chloride. It forms a dark-brown solution with caustic potash, and is separated by hydrochloric or sulphuric acids, but not by nitric acid. It dissolves in ammonia, but not in alkaline carbonates.

Sepia is prepared in commerce by saturating the dried

cuttlefish ink with caustic alkali solution, adding more alkali, boiling for half an hour, filtering and precipitating with an acid, washing and drying at a gentle heat. It is a fine dark brown, used principally in water, and for monochrome work.

Warm Sepia is prepared by the addition of a redder brown, as one of the ferric oxide colours.

Roman Sepia is sepia mixed with a yellow-brown.

Indian Yellow.

Indian yellow (Purree, Piuri, Pioury) is a peculiar pigment of animal origin, used by the natives of India, and to some extent by artists. It is a fairly bright yellow, but not so fine a colour as gamboge, and is found in commerce as round balls weighing a few ounces. Externally it is of a brown or dirty green colour, but bright yellow inside, and with a characteristic urinous smell, which is easily accounted for.

Indian yellow is obtained by collecting the urine of cows fed on the leaf of the mango plant (*Mangifera indica*), and inspissating it until the yellow separates, when it is collected, partially dried over a charcoal fire, and then in the air. The cows are trained only to micturate when the *labiæ majoræ* are stroked, and by this means about 3·5 litres of urine per cow are collected daily. This amount yields about 50 grams of purree.

Purree consists principally of the magnesium and calcium salts of euxanthic acid, $C_{19}H_{18}OH$.

Græbe, who did a good deal of work on this pigment, gives the composition of a fine sample examined by him as

Euxanthic acid	51·0
Silicic acid and alumina	1·5
Magnesium	4·2
Calcium	3·4
Water and volatile matter	39·0
	99·1

The value of this pigment appears to depend on the proportion of euxanthic acid present. Some samples contain a considerable amount of *euxanthone*, $C_{13}H_8O_4$, which is a pale yellow substance, whereas the acid and its salts are of a bright yellow colour.

The composition of five samples, apparently from MM. Lefranc et Cie, of Paris, is given in Thorpe's *Dictionary of Applied Chemistry*:—

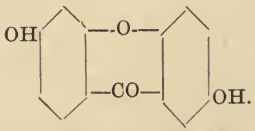
Euxanthic acid	72·3	70·96	4·35	9·3	33·34
Euxanthone .	0·0	1·12	2·80	7·4	34·00
Mg . . .	5·35	4·88	4·85	4·60	3·70
Ca . . .	1·75	2·43	2·61	3·33	3·70

As the quality goes down the proportion of magnesium euxanthate steadily decreases, and the euxanthone increases.

On treating Indian yellow with dilute hydrochloric acid, and then removing the bases with ammonium carbonate, a solution of ammonium euxanthate is obtained, from which hydrochloric acid precipitates crystalline euxanthic acid. Melting-point, 156° to 158° (with decomposition). On decomposition by boiling with dilute acids, *dextro*-glucuronic acid and euxanthone are formed:—

$$C_{19}H_{18}O_{11} = C_{13}H_8O_4 + C_6H_{10}O_7.$$

Dextro-glucuronic acid is $CHO(CHOH)_4{\cdot}CO_2H$, and according to Græbe euxanthone is represented by the formula



Euxanthic acid would appear to be a glucoside-like compound of euxanthone. Against this constitution the fact that euxanthic acid forms two series of salts, $C_{19}H_{17}O_{11}M'$ and $C_{19}H_{16}O_{11}M'_2$, would appear to militate.

The magnesium salt, which is the principal constituent of purree, is $C_{19}H_{16}O_{11}Mg, 5H_2O$.

Indian yellow was formerly believed by some (Stenhouse, for example) to be of vegetable origin, but this view is evidently erroneous, as its place of manufacture, Monghyr, in Bengal Province, is known. We believe that the peculiar feeding which results in the formation of this colour is not for the benefit of the cows used, and that they do not survive the treatment for long, unless occasionally put off the mango feed.

Indian yellow is only used for water colour.

Bitumen, Asphaltum, Mummy.

Asphaltum or bitumen was originally obtained from the neighbourhood of the Dead Sea, and is a kind of pitch similar to that now obtained in great quantity from the great pitch lake, Trinidad. From its nature it can only be used in oil painting. It is a blackish-brown which both darkens in colour and cracks on the painted surface. It is, therefore, though once used to a considerable extent, an unsuitable pigment for permanent work. Much of the pitch used for black tar, varnishes and japans is now obtained from coal tar, being the residue left in the retort after the distillation of this substance. According to the extent to which the distillation is carried it is known as "hard" or "soft" pitch, and for protective work is usually dissolved in light oils which soon evaporate and leave a black glossy surface.

Mummy is a bituminous product associated with animal remains and derives its rather gruesome name from its source, the bituminous matter having been used in the process of embalming, and probably altered somewhat in character through lapse of time. It is used in oil by artists and is less liable to change than asphaltum. It has probably, in keeping so long, reached its limits of change.

INDEX.

A.

Abney's, Sir W., experiments, 27, 31.
Alizarin, 16, 207, 211, 212.
— lakes, 211.
Alkannin, 235.
Amplitude of waves, 2.
Anchusic acid, 234.
Anthrapurpurin, 213.
Arsenic greens, 157.
— sulphides, 179.
— yellows, 179.
Asphaltum, 275.
Aureolin, 28, 153.
Aureosin, 256.
Azines, 248.
Azo compounds, 250.
Azorubine, 15.

B.

Barium sulphate, 99.
Barytes, 99.
Bistre, 176.
Bitumen, 275.
Black, ivory, 45, 174.
— lamp, 175.
Blanc fixe, 99.
Blue, alizarin, 216.
aniline, 261.
— Antwerp, 32.
— Celestial, 44, 45, 192.
— Chinese, 45.
— copper, 163.
— diphenylamine, 261.
— indigo, 262.
— Prussian, 28, 32, 144, 182.
— ultramarine, 164.
Brazilein, 232.
Brazilin, 232.
Brown, Cappagh, 140.
— Prussian, 144.
Brown, purple, 141.
— Vandyck, 32, 44, 180.

C.

Carbon pigments, 173.
Cardinal, 252.
Carmine, 28, 32.
— lake, 32, 197, 210.
Chocolate, 141.
Chromates, 116.
— analysis of, 123.
Chrome yellow, 32.
Chromium oxide, 32, 113.
Chrysoidine, 252.
Cobalt, 32.
— brown, 149.
— colours, 147.
— oxide, 148.
— pink, 149.
— silicates, 151.
Cœrulein, 259.
Cœruleum, 149.
Coloured bodies, 1, 9.
Colours, oil, 61.
— primary and complementary, 8.
— water, 53.
Copper pigments, 153.
Crimson lakes, 28, 32, 203.
Crocein, 253.

D.

Dichroism, 11.
Diorcellinic acid, 238.
Dispersion, irrationality of, 6.

E.

Enamels, 68, 71.
Encaustic painting, 60.
Eosin, 16, 254.
Erythrin, 237, 238.

Erythrol, 237.
Erythrosin, 256.
Eurhodines, 249.
Euxanthic acid, 274.
Euxanthone, 274.

F.

Factory Act, as applied to white lead, 82.
Flavopurpurin, 214.
Frauenhöfer's lines, 3, 4.
Fresco painting, 56.
Fuchsia, 249.
Fuchsine, 13.

G.

Gallein, 261.
Gamboge, 28, 270.
Garancin, 206.
Giallolino, 177.
Glass, stained and painted, 72.
Green, acid, 16, 259.
— arsenical, 157.
— bice, 154.
— Bremen, 155.
— Brunswick, 45, 126, 162.
— copper, 153.
— emerald, 32, 157.
— ethyl, 259.
— Guignet's, 114.
— iodine, 259.
— malachite, 259.
— methyl, 258.
— Mittler's, 114.
— mountain, 154.
— Paris, 157.
— sap, 231.
— Scheele's, 157.
— Schweinfurt, 157.
— verdigris, 160.
Grenadin, 245.

H.

Hæmatin, 219.
Hæmatoxylin, 217.

I.

Indian red, 28, 32, 44, 133.
Indican, 265.
Indigo, 17, 32, 262.
— purple, 265.
— white, 264.
Indigotin, 263.
Iron oxide pigments, 128.
— — — analysis of, 145.
Isorubin, 244.

K.

Keramic art, 66.

L.

Laccainic acid, 205.
Lakes, alizarin, 211, 257.
— alkanet, 210, 234.
— archil, 210, 237.
— artificial, 242.
— azine, 248.
— azo, 250.
— blue, 258.
— Brazil wood, 209, 232.
— Campeachy, 210, 217.
— carmine, 32, 197, 210.
— coal tar, 239.
— cochineal, 196.
— crimson, 28, 32, 203.
— eosin, 254.
— eurhodine, 249.
— green, 256.
— lac dye, 205.
— logwood, 210, 217.
— madder, 32, 206.
— magenta, 245.
— natural, 194.
— orange, 257.
— orchil, 210, 237.
— quercitron, 221.
— red, 242.
— rhamnus, 225.
— rhodamine, 246.
— safranine, 248.
— scarlet, 32, 206.
— Venice, 210.
— violet, 261.
— yellow, 257.
Laurie, A. P., on white lead, 78.
Laws of refraction, 9.
Lead chromates, 116, 117, 119.
— orange, 40, 43, 119.
— red, 40, 43, 100.
— white, 41, 43, 77.

Light, diffused, 10.
— nature of, 1.
— synthesis of, 7.
— white, 2.
Litharge, 102.
Lithopone, 41, 43.
Lokao, 231.

M.

Magenta, 243.
— new, 244.
Malachite, 154.
Mandarin, 157.
Maroon, 245.
Mars colours, 143.
Massicot, 102.
Mercuric chromate, 123.
— iodide, 112.
Methyl green, 258.
Minium, 100.
Mosaic, 76.
Mummy, 275.

N.

Naples yellow, 176.

O.

Ochres, 128.
— red, 132.
— yellow, 32, 129.
Opaque bodies, 9.
Orange eosin, 256.
— lead, 40, 43, 119.
Orcellinic acid, 238.
Orcinol, 238.
Orpiment, 179.

P.

Paints, antifouling, 37.
Pastels, crayon, 49, 50.
Persian berries, 226, 230.
Phloxin, 256.
Picroerythrin, 238.
Pigments, application of, 18, 49.
— artistic uses of, 18 *et seq.*
— decorative uses of, 34 *et seq.*
— protective uses of, 36 *et seq.*
Powders, coloured, 12.
Purple, French, 239.
— indigo, 265.
Purple, oxide, 141.
Purpurin, 213.
Purree, 273.

Q.

Quercetin, 223, 226, 227, 228, 229.
Quercitrin, 222.

R.

Rays, chemical, 5.
— heat, 5.
— light, 5.
— transmitted, 11.
Realgar, 179.
Red, Indian, 28, 32, 44, 133.
— light, 139.
— Magdala, 249.
— oxide, 141.
— scarlet, 40, 43.
— Venetian, 28, 32, 133.
Rhaminose, 226.
Rhamnazin, 227, 229.
Rhamnegin, 227.
Rhamnetin, 227, 229.
Rhamnose, 230.
Rhodamine, 243, 246.
Rosaniline, 230.
Russell, Dr. (see Abney).

S.

Safranines, 248.
Santaline, 209.
Sap green, 231.
Scarlet, Biebrich, 254.
— naphthalene, 249.
— R., 15.
— royal, 112.
Sepia, 28, 272.
Siennas, 134.
— burnt, 32, 46, 136.
— raw, 32, 135.
Silver chromate, 122.
Smaltine, 151.
Smith, H., experiments on paints, 38.
Spectra absorption, 14.
Spectral colours, simple nature of, 7.
Spectrum, 2, 6.
— invisible, 4.
— normal, 5, 6.

T.

Tartrazine, 16, 258.
Tempera painting, 55.
Terra verte, 32, 143.
Thioflavine, 258.
Transparent bodies, 9.
Triphenyl-methane derivatives, 243.

U.

Ultramarine, 32, 46, 164.
Umbers, 134.
— burnt, 32, 138.
— raw, 137.
— Turkey, 45, 137.

V.

Vandyck brown, 32, 180.
Varnishes, asphaltic, 37.
— oil, 37.
Venetian red, 28, 32, 133.
Verdigris, 160.
Vermilion, 28, 32, 103.
Vermilionette, 40, 43, 108, 112.
Violet, methyl, 17.
Vividian, 114.

W.

Water colours, action of light on, 27, 31.
Wave length, 2.
White, enamel, 99.
Whitening, 99.

X.

Xanthorhamnin, 228.

Y.

Yellow, cadmium, 180.
— Indian, 273.
— Naples, 176.
— ochre, 32, 129.
— royal, 179.
— Turner's, 177.

LIBRARY OF THE UNIVERSITY OF CALIFORNIA

THE ABERDEEN UNIVERSITY PRESS LIMITED.

SEPTEMBER, 1901.

This Catalogue cancels all former editions.

The Publishers seek to issue thoroughly helpful works. These books in every instance will, they believe, be found of good value. Employers will do well to place copies of these books in the hands of the bright and promising young men in their employ, in order the better to equip them to become increasingly useful as employees. A workman who uses his brains must be preferable to one who does not *think* about his work. Brains require stimulus. These books provide that stimulus.

A Catalogue

OF

Special Technical Works

FOR

MANUFACTURERS, PROFESSIONAL MEN, STUDENTS, COLLEGES AND TECHNICAL SCHOOLS

BY EXPERT WRITERS

FOR THE

OIL, PAINT, COLOUR VARNISH, SOAP, CHEMICAL, TEXTILE, LEATHER, PAPER, COLLIERY, POTTERY, GLASS, PLUMBING AND DECORATING TRADES AND SCIENTIFIC PROFESSIONS.

PUBLISHED BY

SCOTT, GREENWOOD & CO.,

PUBLISHERS OF TECHNICAL BOOKS,

19 LUDGATE HILL, LONDON, E.C.

Tel. Address: "PRINTERIES, LONDON". **Tel. No. 5403, Bank.**

N.B.—*Full Particulars of Contents of any of the following books sent post free on application.*

Messrs. Scott, Greenwood & Co. are open to make offers for the publication of technical works.

Books on Oils, Soaps, Colours, Chemicals, Glue, Varnishes, etc.

THE PRACTICAL COMPOUNDING OF OILS, TALLOW AND GREASE FOR LUBRICATION, ETC.

By An Expert Oil Refiner. 100 pp. 1898. Demy 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., **Introductory Remarks** on the General Nomenclature of Oils, Tallow and Greases suitable for Lubrication.—II., **Hyrocarbon Oils.**—III., **Animal and Fish Oils.**—IV., **Compound Oils.**—V., **Vegetable Oils.**—VI.. **Lamp Oils.**—VII., **Engine Tallow, Solidified Oils and Petroleum Jelly.**—VIII., **Machinery Greases: Loco and Anti-friction.**—IX., **Clarifying and Utilisation of Waste Fats, Oils, Tank Bottoms, Drainings of Barrels and Drums, Pickings Up, Dregs, etc.**—X., **The Fixing and Cleaning of Oil Tanks, etc.**—**Appendix and General Information.**

Press Opinions.

"This work is written from the standpoint of the oil trade, but its perusal will be found very useful by users of machinery and all who have to do with lubricants in any way."—*Colliery Guardian.*

"The properties of the different grades of mineral oil and of the animal and vegetable non-drying oils are carefully described, and the author justly insists that the peculiarities of the machinery on which the lubricants are to be employed must be considered almost before everything else. . . . The chapters on grease and solidified oils, etc., are excellent."—*The Ironmonger.*

SOAPS. A Practical Manual of the Manufacture of Domestic, Toilet and other Soaps. By George H. Hurst, F.C.S. Illustrated with Sixty-six Engravings. 390 pp. 1898. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Chapters I., **Introductory.**—II., **Soap-maker's Alkalies.**—III., **Soap Fats and Oils.**—IV., **Perfumes.**—V., **Water as a Soap Material.**—VI., **Soap Machinery.**—VII., **Technology of Soap-making.**—VIII., **Glycerine in Soap Lyes.**—IX., **Laying out a Soap Factory.**—X., **Soap Analysis.**—**Appendices.**

Press Opinions.

"We think it is the most practical book on these subjects that has come to us from England so far."—*American Soap Journal.*

"Much useful information is conveyed in a convenient and trustworthy manner which will appeal to practical soap-makers."—*Chemical Trade Journal.*

"Works that deal with manufacturing processes, and applied chemistry in particular, are always welcome. Especially is this the case when the material presented is so up-to-date as we find it here."—*Bradford Observer.*

"The best and most reliable methods of analysis are fully discussed, and form a valuable source of reference to any works' chemist. . . . Our verdict is a capitally produced book, and one that is badly needed."—*Birmingham Post.*

ANIMAL FATS AND OILS: Their Practical Production, Purification and Uses for a great Variety of Purposes. Their Properties, Falsification and Examination. A Handbook for Manufacturers of Oil and Fat Products, Soap and Candle Makers, Agriculturists, Tanners, Margarine Manufacturers, etc., etc. By Louis Edgar Andés. Sixty-two Illustrations. 240 pp. 1898. Demy 8vo. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Introduction. Occurrence, Origin, Properties and Chemical Constitution of Animal Fats Preparation of Animal Fats and Oils. Machinery. Tallow-melting Plant. Extraction Plant. Presses. Filtering Apparatus. Butter: Raw Material and Preparation, Properties, Adulterations, Beef Lard or Remelted Butter, Testing. Candle-fish Oil. Mutton-Tallow. Hare Fat. Goose Fat. Neatsfoot Oil. Bone Fat: Bone Boiling, Steaming Bones, Extraction, Refining. Bone Oil. Artificial Butter: Oleomargarine, Margarine Manufacture in France, Grasso's Process, "Kaiser's Butter," Jahr & Münzberg's Method, Filbert's Process, Winter's Method. Human Fat. Horse Fat. Beef Marrow. Turtle Oil. Hog's Lard: Raw Material, Preparation, Properties, Adulterations, Examination. Lard Oil. Fish Oils. Liver Oils. Artificial Train Oil. Wool Fat: Properties, Purified Wool Fat. Spermaceti: Examination of Fats and Oils in General.

Press Opinions.

"The descriptions of technical processes are clear, and the book is well illustrated and should prove useful."—*Manchester Guardian.*

"It is a valuable work, not only for the student, but also for the practical manufacturer of oil and fat products."—*Journal of the American Chemical Society.*

"The work is very fully illustrated, and the style throughout is in strong contrast to that employed in many such treatises, being simple and clear."—*Shoe and Leather Record.*

"An important handbook for the 'fat industry,' now a large one. The explanation of the most scientific processes of production lose nothing of their clearness in the translation."—*Newcastle Chronicle.*

"The latest and most improved forms of machinery are in all cases indicated, and the many advances which have been made during the past years in the methods of producing the more common animal fats—lard, tallow and butter—receive due attention."—*Glasgow Herald.*

VEGETABLE FATS AND OILS: Their Practical Preparation, Purification and Employment for Various Purposes, their Properties, Adulteration and Examination. A Handbook for Oil Manufacturers and Refiners, Candle, Soap and Lubricating Oil Makers, and the Oil and Fat Industry in General. Translated from the German of Louis Edgar Andés. 94 Illustrations. 320 pp. 1897. Demy 8vo. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Statistical Data. General Properties of the Vegetable Fats and Oils. Estimation of the Amount of Oil in Seeds. Table of Vegetable Fats and Oils, with French and German Nomenclature, Source and Origin and Percentage of Fat in the Plants from which they are Derived. The Preparation of Vegetable Fats and Oils: Storing Oil Seeds; Cleaning the Seed. Apparatus for Grinding Oil Seeds and Fruits. Installation of Oil and Fat Works. Extraction Method of Obtaining Oils and Fats. Oil Extraction Installations. Press Moulds. Non-drying Vegetable Oils. Vegetable drying Oils. Solid Vegetable Fats. Fruits Yielding Oils and Fats. Wool-softening Oils. Soluble Oils. Treatment of the Oil after Leaving the Press Improved Methods of Refining with Sulphuric Acid and Zinc Oxide or Lead Oxide. Refining with Caustic Alkalies, Ammonia, Carbonates of the Alkalies, Lime. Bleaching Fats and Oils. Practical Experiments on the Treatment of Oils with regard to Refining and Bleaching. Testing Oils and Fats.

Press Opinions.

"Concerning that and all else within the wide and comprehensive connection involved, this book must be invaluable to every one directly or indirectly interested in the matters it treats of."—*Commerce.*

"The proprietors of the *Oil and Colourman's Journal* have not only placed a valuable and highly interesting book of reference in the hands of the fats and oils industry in general, but have rendered no slight service to experimental and manufacturing chemists."—*Manufacturing Chemist.*

IRON-CORROSION, ANTI-FOULING AND ANTI-CORROSIVE PAINTS. By Louis Edgar Andés. 62 Illustrations. 275 pp. Translated from the German. Demy 8vo. 1900. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Ironrust and its Formation—Protection from Rusting by Paint—Grounding the Iron with Linseed Oil, etc.—Testing Paints—Use of Tar for Painting on Iron—Anti-corrosive Paints—Linseed Varnish—Chinese Wood Oil—Lead Pigments—Iron Pigments—Artificial Iron Oxides—Carbon—Preparation of Anti-corrosive Paints—Results of Examination of Several Anti-corrosive Paints—Paints for Ship's Bottoms—Anti-fouling Compositions—Various Anti-corrosive and Ship's Paints—Official Standard Specifications for Ironwork Paints—Index.

Press Opinions.

"This is a very valuable book, translated from the German, discussing in detail anti-fouling and anti-corrosive paints."—*British Mercury.*

"Will be of great service to paint manufacturers, engineering contractors, ironfounders, shipbuilders and others."—*Engineer and Iron Trades Advertiser.*

"The book before us deals with the subject in a manner at once practical and scientific, and is well worthy of the attention of all builders, architects and engineers."—*The Builder.*

"The book is very readable and full of valuable information, and bearing in mind the importance of the subject treated, it is one which engineers will be well advised to procure at an early date."—*Railway Engineer.*

"The author goes fully into his subject, and the translator has been successful in reproducing in another language what he has to say. There are given in the text numerous illustrations of the rusting of iron, prepared in the course of a series of personal experiments on the formation of rust."—*Journal of Gas Lighting.*

"This work is a very elaborate and useful record of the various phenomena in connection with the corrosion of iron and its protection against corrosion. . . . The book is an exceedingly useful record of what has been done in connection with iron preservation, and will undoubtedly prove to be of much value to railway engineers, shipowners, etc."—*Fairplay.*

"Herr Andés' book, written purely from a scientific standpoint, will be particularly useful to iron manufacturers, shipbuilders and shipowners. . . . The book is beautifully printed on good paper, and its appearance does credit to the publishers; the work of translation has been remarkably well done, the language bearing none of those irritating traces of Teutonism which disfigure so many English versions of German technical works."—*The Ironmonger.*

"This knowledge is conveyed with characteristic German thoroughness in this useful work of Herr Andés, which loses nothing of clearness in Mr. Salter's excellent translation. The causes of rust formation are examined, the proper methods of cleansing the ironwork detailed, and the constitution and application of suitable preventative coverings explained. . . . The book is a welcome contribution to technological literature, and will be found worthy of the careful study of all who are professionally engaged in the arrangement or superintendence of the class of work dealt with."—*Western Daily Mercury.*

"The author explains the nature of rust and its formation, and the text is illustrated from about fifty photographs. An immense amount of carefully arranged information follows as to the best methods of applying anti-corrosive substances and the various pigments most efficacious for use under all circumstances. The author has evidently thoroughly investigated and mastered the subject of iron corrosion, its cause and its prevention; and we regard his book as of the greatest importance to bridge-builders and makers and users of structural iron and steel. The book is illustrated throughout and is admirably indexed and arranged."—*Iron and Steel Trades Journal.*

THE MANUFACTURE OF ALUM AND THE SULPHATES AND OTHER SALTS OF ALUMINA AND IRON. Their Uses and Applications as Mordants in Dyeing and Calico Printing, and their other Applications in the Arts, Manufactures, Sanitary Engineering, Agriculture and Horticulture. Translated from the French of LUCIEN GESCHWIND. 195 Illustrations. Nearly 400 pp. Royal 8vo. 1901. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Part I., **Theoretical Study of Aluminium, Iron, and Compounds of these Metals.**—Chapters I., Aluminium and its Compounds.—II., Iron and Iron Compounds.

Part II., **Manufacture of Aluminium Sulphates and Sulphates of Iron.**—Chapters III., Manufacture of Aluminium Sulphate and the Alums.—IV., Manufacture of Sulphates of Iron.

Part III., **Uses of the Sulphates of Aluminium and Iron.**—Chapters V., Uses of Aluminium Sulphate and Alums—Application to Wool and Silk—Preparing and using Aluminium Acetates—Employment of Aluminium Sulphate in Carbonising Wool—The Manufacture of Lake Pigments—Manufacture of Prussian Blue—Hide and Leather Industry—Paper Making—Hardening Plaster—Lime Washes—Preparation of Non-inflammable Wood, etc.—Purification of Waste Waters.—VI., **Uses and Applications of Ferrous Sulphate and Ferric Sulphates.**—Dyeing—Manufacture of Pigments—Writing Inks—Purification of Lighting Gas—Agriculture—Cotton Dyeing—Disinfectant—Purifying Waste Liquors—Manufacture of Nordhausen Sulphuric Acid—Fertilising.

Part IV., **Chemical Characteristics of Iron and Aluminium.—Analysis of Various Aluminous or Ferruginous Products.**—Chapter VII., Aluminium.—**Analysing Aluminium Products.**—Alunite Alumina—Sodium Aluminate—Aluminium Sulphate. Chapter VIII., **Iron.**—Analytical Characteristics of Iron Salts—Analysis of Pyritic Lignite—Ferrous and Ferric Sulphates—Rouil Mordant—Index.

MANUAL OF AGRICULTURAL CHEMISTRY. By HERBERT INGLE, F.I.C., Lecturer on Agricultural Chemistry, the Yorkshire College; Lecturer in the Victoria University. [*In the press.*

Contents.

Chapters I., Introduction.—II., The Atmosphere.—III., The Soil.—IV., The Reactions occurring in Soils.—V., The Analysis of Soils.—VI., Manures, Natural.—VII., Manures (continued).—VIII., The Analysis of Manures.—IX., The Constituents of Plants.—X., The Plant.—XI., Crops.—XII., The Animal.

LUBRICATING OILS, FATS AND GREASES: Their Origin, Preparation, Properties, Uses and Analyses. A Handbook for Oil Manufacturers, Refiners and Merchants, and the Oil and Fat Industry in General. By GEORGE H. HURST, F.C.S. Second Edition. Sixty-five Illustrations. 313 pp. Demy 8vo. 1901. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Chapters I., **Introductory.** Oils and Fats, Fatty Oils and Fats, Hydrocarbon Oils, Uses of Oils.—II., **Hydrocarbon Oils.** Distillation, Simple Distillation, Destructive Distillation, Products of Distillation, Hydrocarbons, Paraffins, Olefins, Napthenes.—III., **Scotch Shale Oils.** Scotch Shales, Distillation of Scotch Oils, Shale Retorts, Products of Distilling Shales

Separating Products, Treating Crude Shale Oil, Refining Shale Oil, Shale Oil Stills, Shale Naphtha Burning Oils, Lubricating Oils, Wax.—IV., **Petroleum.** Occurrence, Geology, Origin, Composition, Extraction, Refining, Petroleum Stills, Petroleum Products, Cylinder Oils, Russian Petroleum, Deblooming Mineral Oils.—V., **Vegetable and Animal Oils.** Introduction, Chemical Composition of Oils and Fats, Fatty Acids, Glycerine, Extraction of Animal and Vegetable Fats and Oils, Animal Oils, Vegetable Oils, Rendering, Pressing, Refining, Bleaching, Tallow, Tallow Oil, Lard Oil, Neatsfoot Oil, Palm Oil, Palm Nut Oil, Cocoanut Oil, Castor Oil, Olive Oil, Rape and Colza Oils, Arachis Oil, Niger Seed Oil, Sperm Oils, Whale Oil, Seal Oil, Brown Oils, Lardine, Thickened Rape Oil.—VI., **Testing and Adulteration of Oils.** Specific Gravity, Alkali Tests, Sulphuric Acid Tests, Free Acids in Oils, Viscosity Tests, Flash and Fire Tests, Evaporation Tests, Iodine and Bromide Tests, Elaidin Test, Melting Point of Fat, Testing Machines.—VII., **Lubricating Greases.** Rosin Oil, Anthracene Oil, Making Greases, Testing and Analysis of Greases.—VIII., **Lubrication.** Friction and Lubrication, Lubricant, Lubrication of Ordinary Machinery, Spontaneous Combustion of Oils, Stainless Oils, Lubrication of Engine Cylinders, Cylinder Oils.—**Appendices.** A. Table of Baume's Hydrometer—B. Table of Thermometric Degrees—C. Table of Specific Gravities of Oils—**Index.**

Press Opinions.

"The book is well printed, and is a credit alike to author, printer and publisher."—*Textile Mercury.*

"It will be a valuable addition to the technical library of every steam user's establishment."—*Machinery Market.*

"Mr. Hurst has in this work supplied a practical treatise which should prove of especial value to oil dealers, and also, though in a less degree, to oil users."—*Textile Manufacturer.*

"This is a clear and concise treatment of the method of manufacturing and refining lubricating oils. . . . The book is one which is well worthy the attention of readers who are users of oil."—*Textile Recorder.*

"We have no hesitation in saying that in our opinion this book ought to be very useful to all those who are interested in oils, whether as manufacturers or users of lubricants, or to those chemists or engineers whose duty it may be to report upon the suitability of the same for any particular class of work."—*Engineer.*

"The author is widely known and highly respected as an authority on the chemistry of oils and the technics of lubrication, and it is safe to say that no work of similar interest or equal value to the general oil-selling and consuming public has heretofore appeared in the English language."—*Drugs, Oils and Paints,* U.S.A.

"This valuable and useful work, which is both scientific and practical, has been written with a view of supplying those who deal in and use oils, etc., for the purpose of lubrication, with some information respecting the special properties of the various products which cause these various oils to be of value as lubricants."—*Industries and Iron.*

"A mere glance at the table of contents is sufficient to show how various are the conditions to which these materials have to be applied, how much knowledge is required for the selection of the right kind for each particular purpose, and how by processes of mixture or manufacture the requisite qualities are obtained in each case."—*Manchester Guardian.*

AMMONIA AND ITS COMPOUNDS: Their Manufacture and Uses.

By CAMILLE VINCENT, Professor at the Central School of Arts and Manufactures, Paris. Translated from the French by M. J. SALTER. Royal 8vo. 113 pp. 1901. Thirty-two Illustrations. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Chapters I., **General Considerations:** Sections 1. Various Sources of Ammoniacal Products; 2. Human Urine as a Source of Ammonia. II., **Extraction of Ammoniacal Products from Sewage:** Sections 1. Preliminary Treatment of Excreta in the Settling Tanks—The Lencauchez Process, The Bilange Process, The Kuentz Process; 2. Treatment of the Clarified Liquors for the Manufacture of Ammonium Sulphate—The Figuera Process and Apparatus, Apparatus of Margueritte and Sourdeval, The Lair Apparatus, Apparatus of Sintier and Muhé, Apparatus of Bilange, The Kuentz Process, Process and Apparatus of Hennebutte and De Vauréal; 3. Treatment of Entire Sewage—Chevalet's Apparatus, Paul Mallet's Apparatus, Lencauchez's Apparatus. III., **Extraction of Ammonia from Gas Liquor:** Sections 1. Clarification of Gas Liquor; 2. Manufacture of Ammonium Sulphate—A. Mallet's Apparatus, A. Mallet's Modified Apparatus, Paul Mallet's Apparatus, Chevalet's Apparatus, Grüneberg's Apparatus; 3. Concentration of Gas Liquor—Solvay's Apparatus, Kuentz's Apparatus, Grüneberg's Apparatus. IV., **Manufacture of Ammoniacal Compounds from Bones, Nitrogenous Waste, Beetroot Wash and Peat:** Sections 1. Ammonia from Bones; 2. Ammonia from Nitrogenous Waste Materials; 3. Ammonia from Beetroot Wash (Vinasse); 4. Ammonia from Peat—Treatment of the Ammoniacal Liquors. V., **Manufacture of Caustic Ammonia, and Ammonium Chloride, Phosphate and Carbonate:** Sections 1. Manufacture of Caustic Ammonia; 2. Manufacture of Ammonium Chloride—From Fermented Urine, Process of the Lesage Company, Kuentz's Process; From Gas Liquor, English Process, Kuentz's Process; From the Dry Distillation of Animal Matter; From Ammonium Sulphate, Sublimation; 3. Ammonium Phosphates; 4. Carbonates of Ammonium—Sesquicarbonate from Animal Matter, English Process, Uses. VI., **Recovery of Ammonia from the Ammonia-Soda Mother Liquors:** Sections 1. General Considerations; 2. Apparatus of Schlœsing and Rolland; 3. Apparatus of the Société Anonyme de l'Est.—**Index.**

THE MANUFACTURE OF VARNISHES, OIL REFINING AND BOILING, AND KINDRED INDUSTRIES. Describing the Manufacture of Spirit Varnishes and Oil Varnishes; Raw Materials: Resins, Solvents and Colouring Principles; Drying Oils: their Properties, Applications and Preparation by both Hot and Cold Processes; Manufacture, Employment and Testing of Different Varnishes. Translated from the French of ACH. LIVACHE, Ingénieur Civil des Mines. Greatly Extended and Adapted to English Practice, with numerous Original Recipes. By JOHN GEDDES MCINTOSH, Lecturer on Oils, Colours and Varnishes, Regent Street Polytechnic. Twenty-seven Illustrations. 400 pp. Demy 8vo. 1899. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

I. Resins: Gum Resins, Oleo Resins and Balsams, Commercial Varieties, Source, Collection, Characteristics, Chemical Properties, Physical Properties, Hardness, Adulterations. Appropriate Solvents, Special Treatment, Special Use.—II. Solvents: Natural, Artificial, Manufacture, Storage, Special Use.—III. Colouring: Principles, (1) Vegetable, (2) Coal Tar, (3) Coloured Resinates, (4) Coloured Oleates and Linoleates.—Gum Running: Furnaces, Bridges, Flues, Chimney Shafts, Melting Pots, Condensers, Boiling or Mixing Pans, Copper Vessels, Iron Vessels (Cast), Iron Vessels (Wrought), Iron Vessels (Silvered), Iron Vessels Enamelled), Steam Superheated Plant, Hot-air Plant.—Spirit Varnish Manufacture: Cold Solution Plant, Mechanical Agitators, Hot Solution Plant, Jacketted Pans, Mechanical Agitators, Clarification and Filtration, Bleaching Plant, Storage Plant.—Manufacture, Characteristics and Uses of the Spirit Varnishes yielded by: Amber, Copal, Dammar, Shellac, Mastic, Sandarac, Rosin, Asphalt, India Rubber, Gutta Percha, Collodion, Celluloid, Resinates, Oleates.—Manufacture of Varnish Stains.—Manufacture of Lacquers.—Manufacture of Spirit Enamels.—Analysis of Spirit Varnishes.—Physical and Chemical Constants of Resins.—Table of Solubility of Resins in different Menstrua.—Systematic qualitative Analysis of Resins, Hirschop's tables.—Drying Oils: Oil Crushing Plant, Oil Extraction Plant, Individual Oils, Special Treatment of Linseed Oil, Poppyseed Oil, Walnut Oil, Hempseed Oil, Llamantia Oil, Japanese Wood Oil, Gurjun Balsam, Climatic Influence on Seed and Oil.—Oil Refining: Processes, Thenard's, Liebig's, Filtration, Storage, Old Tanked Oil.—Oil Boiling: Fire Boiling Plant, Steam Boiling Plant, Hot-Air Plant, Air Pumps, Mechanical Agitators, Vincent's Process, Hadfield's Patent, Storer's Patent, Walton's Processes, Continental Processes, Pale Boiled Oil, Double Boiled Oil, Hartley and Blenkinsop's Process.—Driers: Manufacture, Special Individual Use of (1) Litharge, (2) Sugar of Lead, (3) Red Lead, (4) Lead Borate, (5) Lead Linoleate, (6) Lead Resinate, (7) Black Oxide of Manganese, (8) Manganese Acetate, (9) Manganese Borate, (10) Manganese Resinate, (11) Manganese Linoleate, Mixed Resinates and Linoleates, Manganese and Lead, Zinc Sulphate, Terebine, Liquid Driers.—Solidified Boiled Oil.—Manufacture of Linoleum.—Manufacture of India Rubber Substitutes.—Printing Ink Manufacture—Lithographic Ink Manufacture.—Manufacture of Oil Varnishes.—Running and Special Treatment of Amber, Copal, Kauri, Manilla.—Addition of Oil to Resin.—Addition of Resin to Oil.—Mixed Processes.—Solution in Cold of previously Fused Resin.—Dissolving Resins in Oil, etc., under pressure.—Filtration.—Clarification.—Storage.—Ageing.—Coachmakers' Varnishes and Japans.—Oak Varnishes.—Japanners' Stoving Varnishes.—Japanners' Gold Size.—Brunswick Black.—Various Oil Varnishes.—Oil-Varnish Stains.—Varnishes for "Enamels".—India Rubber Varnishes.—Varnishes Analysis: Processes, Matching.—Faults in Varnishes: Cause, Prevention.—Experiments and Exercises.

Press Opinions.

"There is no question that this is a useful book."—*Chemist and Druggist.*

"The different formulæ which are quoted appear to be far more 'practical' than such as are usually to be found in text-books; and assuming that the original was published two or three years ago, and was only slightly behindhand in its information, the present volume gives a fair insight into the position of the varnish industry."—*The Ironmonger.*

Letter from the Teacher of a Technical Class.

"As a teacher I have often been consulted as to the best work on Varnish Manufacture and kindred industries, and have been at a loss in recommending a really practical one. It is therefore with pleasure that I can now testify as to the merits of the book on these subjects by A. Livache and J. G. McIntosh recently published by Messrs. Scott, Greenwood & Co. In my opinion *no* varnish maker ought to be without it; moreover, it is the best text-book that could be put into the hands of trade students or beginners. It has also the merits of being thoroughly up-to-date and of possessing a remarkably comprehensive index. I can conscientiously recommend it to my students and trade friends."—CHARLES HARRISON, Lecturer on the Manufacture of Painters' Oils, Colours and Varnishes, Borough Polytechnic, Borough Road, S.E.

"23*rd May*, 1899"

THE MANUFACTURE OF LAKE PIGMENTS FROM ARTIFICIAL COLOURS.

By FRANCIS H. JENNISON, F.I.C., F.C.S. **Sixteen Coloured Plates, showing Specimens of Eighty-nine Colours, specially prepared from the Recipes given in the Book.** 136 pp. Demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Introduction.—II., The Groups of the Artificial Colouring Matters.—III., The Nature and Manipulation of Artificial Colours.—IV., Lake-forming Bodies for Acid Colours.—V., Lake-forming Bodies' Basic Colours.—VI., Lake Bases.—VII., The Principles of Lake Formation.—VIII., Red Lakes.—IX., Orange, Yellow, Green, Blue, Violet and Black Lakes.—X., The Production of Insoluble Azo Colours in the Form of Pigments.—XI., The General Properties of Lakes Produced from Artificial Colours.—XII., Washing, Filtering and Finishing.—XIII., Matching and Testing Lake Pigments.—Index.

Press Opinions.

"It is evidently the result of prolonged research, and cannot but prove a valuable consulting work to those engaged in the industry."—*Derby Mercury.*

"The practical portion of the volume is the one which will especially commend itself, as that is the part of the subject which most readers would buy the book for."—*Chemist and Druggist.*

"This work just issued is a very valuable treatise on the manufacture of lake pigments of the coal-tar series principally. The plan adopted by the author in writing up the subject enables the manufacture to be very readily understood. . . . The general properties of lakes produced from artificial colours, washing, filtering and finishing, and matching and testing lake pigments are well and exhaustively described, so that no manufacturer or user of lake pigments can well afford to be without this work."—*Chemical Trade Journal.*

"This is undoubtedly a book which will occupy a very high place amongst technical works, and will prove of exceptional value to all whom it immediately concerns. We have no hesitation in recommending it as one of the best works of its class we have ever read. Mr. Jennison has set about his task with a lucid style, and with a complete mastery of his subject. . . We do not think students of the technical side of the paint and colour industry can possibly spend 7s. 6d. in a more profitable way than by buying this publication."—*Eastern Morning News.*

THE TESTING AND VALUATION OF RAW MATERIALS USED IN PAINT AND COLOUR MANUFACTURE.

By M. W. JONES, F.C.S. A Book for the Laboratories of Colour Works. 88 pp. Crown 8vo. 1900. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Aluminium Compounds. China Clay. Iron Compounds. Potassium Compounds. Sodium Compounds. Ammonium Hydrate. Acids. Chromium Compounds. Tin Compounds. Copper Compounds. Lead Compounds. Zinc Compounds. Manganese Compounds. Arsenic Compounds. Antimony Compounds. Calcium Compounds. Barium Compounds. Cadmium Compounds. Mercury Compounds. Ultramarine. Cobalt and Carbon Compounds. Oils Index.

Press Opinions.

"Though this excellent little work can appeal only to a limited class, the chemists in colour works, yet it will appeal to them very strongly indeed, for it will put them on the track of short, rapid, and yet approximately, accurate methods of testing the comparative value of competing samples of raw material used in paint and colour manufacture."—*North British Daily Mail.*

"This little text-book is intended to supplement the larger and more comprehensive works on the subject, and it embodies the result of Mr. Jones' experiments and experiences, extending over a long period. It gives, under separate headings, the principal ingredients and impurities found in the raw materials, and is a handy work of reference for ascertaining what is valuable or detrimental in the sample under examination."—*Blackburn Times.*

"There is no attempt at literary adornment nor straining after literary effect, but the lessons are imparted in simple and concise language. This is just what a text-book should be. . . . The treatise is certainly most useful, and bears internal evidence of being the results of actual work in a busy manufactory and not of ephemeral cramming in a technical school. The chapter arrangement is good, the index satisfactory, and the book is altogether one which the practical chemist should keep as accessible to his crucibles and filter paper."—*Manchester Courier.*

THE CHEMISTRY OF ESSENTIAL OILS AND ARTIFICIAL PERFUMES.

By Ernest J. Parry, B.Sc. (Lond.), F.I.C., F.C.S. Illustrated with Twenty Engravings. 400 pp. 1899. Demy 8vo. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Chapters I., **The General Properties of Essential Oils.**—II., **Compounds occurring in Essential Oils.**—III., **The Preparation of Essential Oils.**—IV., **The Analysis of Essential Oils.**—V., **Systematic Study of the Essential Oils.**—VI., **Terpeneless Oils.**—VII., **The Chemistry of Artificial Perfumes.**—**Appendix:** Table of Constants.

Press Opinions.

"There can be no doubt that the publication will take a high place in the list of scientific text-books."—*London Argus*

"We can heartily recommend this volume to all interested in the subject of essential oils from the scientific or the commercial standpoint."—*British and Colonial Druggist.*

"Mr. Parry has done good service in carefully collecting and marshalling the results of the numerous researches published in various parts of the world."—*Pharmaceutical Journal.*

"At various times monographs have been printed by individual workers, but it may safely be said that Mr. Parry is the first in these latter days to deal with the subject in an adequate manner. His book is well conceived and well written. . . . He is known to have sound practical experience in analytical methods, and he has apparently taken pains to make himself *au fait* with the commercial aspects of the subject."—*Chemist and Druggist.*

"Mr. Parry's reputation as a scientist is fully established, and we can therefore accept any work emanating from his pen as being of the greatest practical value. We have perused the work before us with much care, and are convinced that the contents will be found most serviceable and its publication most opportune. . . . He avoids unnecessary details, but includes everything that is essential to systematic treatment, while he attempts no more 'than to give an outline of the principles involved'. . . . We congratulate Mr. Parry on the scientific value of his work, and hope that if the progress of the colonies in the manufacture of essential oils and perfumes equals what we are justified in expecting, it will become an Australian hand-book, everywhere appreciated."—*The Australian Brewers' Journal.*

DRYING OILS, BOILED OIL AND SOLID AND LIQUID DRIERS.

By L. E. Andés. A Practical Work for Manufacturers of Oils, Varnishes, Printing Inks, Oilcloth and Linoleum, Oilcakes, Paints, etc. Expressly Written for this Series of Special Technical Books, and the Publishers hold the Copyright for English and Foreign Editions. Forty-two Illustrations. 360 pp. 1901. Demy 8vo. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Chapters I., General Chemical and Physical Properties of the Drying Oils; Cause of the Drying Property; Absorption of Oxygen; Behaviour towards Metallic Oxides, etc.—II., The Properties of and Methods for obtaining the Drying Oils.—III., Production of the Drying Oils by Expression and Extraction; Refining and Bleaching; Oil Cakes and Meal; The Refining and Bleaching of the Drying Oils; The Bleaching of Linseed Oil.—IV., The Manufacture of Boiled Oil; The Preparation of Drying Oils for Use in the Grinding of Paints and Artists' Colours and in the Manufacture of Varnishes by Heating over a Fire or by Steam, by the Cold Process, by the Action of Air, and by Means of the Electric Current; The Driers used in Boiling Linseed Oil; The Manufacture of Boiled Oil and the Apparatus therefor; Livache's Process for Preparing a Good Drying Oil and its Practical Application.—V., The Preparation of Varnishes for Letterpress, Lithographic and Copperplate Printing, for Oilcloth and Waterproof Fabrics; The Manufacture of Thickened Linseed Oil, Burnt Oil, Stand Oil by Fire Heat, Superheated Steam, and by a Current of Air.—VI., Behaviour of the Drying Oils and Boiled Oils towards Atmospheric Influences, Water, Acids and Alkalies.—VII., Boiled Oil Substitutes.—VIII., The Manufacture of Solid and Liquid Driers from Linseed Oil and Rosin; Linolic Acid Compounds of the Driers.—IX., The Adulteration and Examination of the Drying Oils and Boiled Oil.

REISSUE OF CHEMICAL ESSAYS OF C. W. SCHEELE.

First Published in English in 1786. Translated from the Academy of Sciences at Stockholm, with Additions. 300 pp. Demy 8vo. 1901. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Memoir: C. W. Scheele and his work (written for this edition).—Chapters I., On Fluor Mineral and its Acid.—II., On Fluor Mineral.—III., Chemical Investigation of Fluor Acid, with a View to the Earth which it Yields, by Mr. Wiegler.—IV., Additional Information Concerning Fluor Minerals.—V., On Manganese, Magnesium, or Magnesia Vitrariorum.—VI., On Arsenic and its Acid.—VII., Remarks upon Salts of Benzoin.—VIII., On Silex, Clay and Alum.—IX., Analysis of the Calculus Vesical.—X., Method of Preparing Mercurius

Dulcis Via Humida.—XI., Cheaper and more Convenient Method of Preparing Pulvis Algarothi.—XII., Experiments upon Molybdæna.—XIII., Experiments on Plumbago.—XIV., Method of Preparing a New Green Colour.—XV., Of the Decomposition of Neutral Salts by Unslaked Lime and Iron.—XVI., On the Quantity of Pure Air which is Daily Present in our Atmosphere.—XVII., On Milk and its Acid.—XVIII., On the Acid of Saccharum Lactis.—XIX., On the Constituent Parts of Lapis Ponderosus or Tungsten.—XX., Experiments and Observations on Ether.

GLUE AND GLUE TESTING. By Samuel Rideal, D.Sc.

Lond., F.I.C. Fourteen Engravings. 144 pp. Demy 8vo. 1900. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Chapters I., **Constitution and Properties:** Definitions and Sources, Gelatine, Chondrin and Allied Bodies, Physical and Chemical Properties, Classification, Grades and Commercial Varieties.—II., **Raw Materials and Manufacture:** Glue Stock, Lining, Extraction, Washing and Clarifying, Filter Presses, Water Supply, Use of Alkalies, Action of Bacteria and of Antiseptics, Various Processes, Cleansing, Forming, Drying, Crushing, etc., Secondary Products.—III., **Uses of Glue:** Selection and Preparation for Use, Carpentry, Veneering, Paper-Making, Bookbinding, Printing Rollers, Hectographs, Match Manufacture, Sandpaper, etc., Substitutes for other Materials, Artificial Leather and Caoutchouc.—IV., **Gelatine:** General Characters, Liquid Gelatine, Photographic Uses, Size, Tanno-, Chrome and Formo-Gelatine, Artificial Silk, Cements, Pneumatic Tyres, Culinary, Meat Extracts, Isinglass, Medicinal and other Uses, Bacteriology.—V., **Glue Testing:** Review of Processes, Chemical Examination, Adulteration, Physical Tests, Valuation of Raw Materials.—VI., **Commercial Aspects.**

Press Opinions.

"This work is of the highest technical character, and gives not only a full and practical account of the raw materials and manufacture of glues, gelatines and similar substances, but gives many hints and information on the use of such substances in veneering, carpentry and many other purposes. Many tests are given for glue in different stages of the progress of its manufacture, and the commercial value of a commodity so much in general use is exemplified by statistics and figures. It is certainly a valuable treatise upon an article for which very little literature in any form has previously been obtainable."—*Carpenter and Builder.*

"Books on the art of glue making are more than usually scarce, and users of that article, as well as those who may be tempted to embark in the industry, should therefore welcome this book by Dr. Samuel Rideal, a Fellow of the Institute of Chemistry, and a leading authority. In this book he has collected the more important facts connected with the manufacture of glue and allied products, and stated the experience he has gained in examining various commercial samples during the past ten years. . . . Dr. Rideal's book must be regarded as a valuable contribution to other technical literature, which manufacturers, merchants and users may study with profit."—*British Trade Journal.*

"This volume is the latest addition to the excellent series of special technical works for manufacturers and professional and commercial men issued by the well-known publishers of *The Oil and Colourman's Journal.* The volume in every way fully maintains the high standard of excellence of the whole series, and deals with the subject of glue making and glue testing in a thoroughly exhaustive manner. Chapters are given on the constitution and properties, and raw material and manufacture, and of the uses of glue, and in this latter respect it will doubtless be information to many readers to learn to what extent glue enters into the manufacture of many commercial products not apparently associated with glue. Exhaustive chapters on the processes and methods of glue testing, and on its commercial aspects, complete this useful and most carefully prepared volume."—*Carriage Builders' Journal.*

TECHNOLOGY OF PETROLEUM: Oil Fields of the World—Their History, Geography and Geology—Annual Production and Development—Oil-well Drilling—Transport. By Henry Neuberger and Henry Noalhat. Translated from the French by J. G. McIntosh. 550 pp. 153 Illustrations. 26 Plates. Royal 8vo. 1901. Price 21s.; India and Colonies, 22s.; Other Countries, 23s. 6d.; strictly net.

Contents.

Part I., **Study of the Petroliferous Strata**—Chapters I., Petroleum—Definition.—II., The Genesis or Origin of Petroleum.—III., The Oil Fields of Galicia, their History.—IV., Physical Geography and Geology of the Galician Oil Fields.—V., Practical Notes on Galician Land Law—Economic Hints on Working, etc.—VI., Roumania—History, Geography, Geology.—VII., Petroleum in Russia—History.—VIII., Russian Petroleum (*continued*)—Geography and Geology of the Caucasian Oil Fields.—IX., Russian Petroleum (*continued*).—X., The Secondary Oil Fields of Europe, Northern Germany, Alsace, Italy, etc.—XI., Petroleum in France.—XII., Petroleum in Asia—Transcaspian and Turkestan Territory—Turkestan—Persia—British India and Burmah—British Burmah or Lower Burmah—China—Chinese Thibet—Japan, Formosa and Saghalien.—XIII., Petroleum in Oceania—Sumatra, Java, Borneo—Isle of Timor—Philippine Isles—New Zealand.—XIV., The United States of America—History.—XV., Physical Geology and Geography of the United States Oil Fields.—XVI., Canadian and other North American Oil Fields.—XVII., Economic Data of Work in North America.—XVIII., Petroleum in the West Indies and South America.—XIX., Petroleum in the French Colonies.

Part II., **Excavations.**—Chapter XX., Hand Excavation or Hand Digging of Oil Wells.

Part III., **Methods of Boring.**—Chapters XXI., Methods of Oil-well Drilling or Boring.—XXII., Boring Oil Wells with the Rope.—XXIII., Drilling with Rigid Rods and a Free-fall—Fabian System.—XXIV., Free-fall Drilling by Steam Power.—XXV., Oil-well Drilling by the Canadian System.—XXVI., Drilling Oil Wells on the Combined System.—XXVII., Comparison between the Combined Fauck System and the Canadian.—XXVIII., The American System of Drilling with the Rope.—XXIX., Hydraulic Boring with the Drill by Hand and Steam Power.—XXX., Rotary Drilling of Oil Wells, Bits, Steel-crowned Tools, Diamond Tools—Hand Power and Steam Power—Hydraulic Sand-pumping.—XXXI., Improvements in and different Systems of Drilling Oil Wells.

Part IV., **Accidents.**—Chapters XXXII., Boring Accidents—Methods of preventing them—Methods of remedying them.—XXXIII., Explosives and the use of the "Torpedo" Levigation.—XXXIV., Storing and Transport of Petroleum.—XXXV., General Advice—Prospecting, Management and carrying on of Petroleum Boring Operations.

Part V., **General Data.—Customary Formulæ.**—Memento. Practical Part. General Data bearing on Petroleum.—Glossary of Technical Terms used in the Petroleum Industry.—Copious Index.

A DICTIONARY OF CHEMICALS AND RAW PRODUCTS USED IN THE MANUFACTURE OF PAINTS, COLOURS, VARNISHES AND ALLIED PREPARATIONS.

By GEORGE H. HURST, F.C.S. Demy 8vo. 380 pp. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

The names of the Chemicals and Raw Products are arranged in alphabetical order, and the description of each varies in length from half to eight pages. The following are some of the articles described and explained: Acetates—Acetic Acid—Acidimetry—Alcohol—Alum—Ammonia—Amber—Animi—Arsenic—Beeswax—Benzol—Bichromates of Potash and Soda—Bleaching Powder—Bone Black—Boric Acid—Brunswick Green—Cadmium Yellow—Carbonates—Carmine—Carnauba Wax—Caustic Potash and Soda—Chrome Colours—Clay—Coal Tar Colours—Copal—Dammar—Drying Oils—Emerald Green—Gamboge—Glue—Glycerine—Gums—Gypsum—Indian Red—Japanese Lacquer—Lac—Lakes—Lamp Black—Lead Compounds—Linseed Oil—Magnesia—Manganese Compounds—Mica—Nitric Acid—Ochres—Orange Lead—Orr's White—Paraffin—Prussian Blue—Rosin Oil—Sepia—Sienna—Smalts—Sodium Carbonate—Sublimed White Lead—Sulphuric Acid—Terra Verte—Testing Pigments—Turpentine—Ultramarine—Umbers—Vermilionettes—White Lead—Whiting—Zinc Compounds.—Appendix: Comparison of Baumé Hydrometer and Specific Gravity for Liquids Lighter than Water—Hydrometer Table for Liquids Heavier than Water—Comparison of Temperature Degrees—Tables for Converting French Metric Weights and Measures into English—Table of the Elements—etc., etc.—Copious Index.

Press Opinions.

"This treatise will be welcomed by those interested in this industry who have not secured the full advantage of a course of scientific training."—*Chemical Trade Journal.*

"In concise and lucid terms almost every ingredient used in paint and colour manufacture is described, together with the methods of testing their intrinsic and chemical value."—*Pontefract Express.*

"Such a book of reference for paint, colour and varnish manufacturers has long been needed, and in Mr. Hurst the publishers have secured a compiler who is not only a well-known authority and expert, but who has the gift of communicating his knowledge in a concise and lucid form."—*Manchester Courier.*

PURE AIR, OZONE AND WATER.

A Practical Treatise of their Utilisation and Value in Oil, Grease, Soap, Paint, Glue and other Industries. By W. B. COWELL. Twelve Illustrations. 1900. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Chapters I., Atmospheric Air; Lifting of Liquids; Suction Process; Preparing Blown Oils; Preparing Siccative Drying Oils.—II., Compressed Air; Whitewash.—III., Liquid Air; Retrocession.—IV., Purification of Water; Water Hardness.—V., Fleshings and Bones.—VI., Ozonised Air in the Bleaching and Deodorising of Fats, Glues, etc.; Bleaching Textile Fibres.—Appendix: Air and Gases; Pressure of Air at Various Temperatures; Fuel; Table of Combustibles; Saving of Fuel by Heating Feed Water; Table of Solubilities of Scale Making Minerals; British Thermal Units Tables; Volume of the Flow of Steam into the Atmosphere; Temperature of Steam.—Index.

Press Opinions.

"This is a valuable work in little space. . . . In arrangement it is a commendable work, and its value is increased by the index which brings the little volume to a close."—*Newcastle Daily Journal.*

"The book is written solely for manufacturers, who, without doubt, will find it exceedingly practical and useful. The volume contains an appendix wherein is given a great many tables, etc., which manufacturers in the trades referred to will find of inestimable value."—*Blackburn Times.*

THE MANUFACTURE OF MINERAL AND LAKE PIGMENTS. Containing Directions for the Manufacture of all Artificial, Artists and Painters' Colours, Enamel, Soot and Metallic Pigments. A Text-book for Manufacturers, Merchants, Artists and Painters. By Dr. JOSEF BERSCH. Translated from the Second Revised Edition by ARTHUR C. WRIGHT, M.A. (Oxon.), B.Sc. (Lond.), formerly Assistant Lecturer and Demonstrator in Chemistry at the Yorkshire College, Leeds. Forty-three Illustrations. 476 pp., demy 8vo. 1901. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Chapters I., Introduction.—II., Physico-chemical Behaviour of Pigments.—III., Raw Materials Employed in the Manufacture of Pigments.—IV., Assistant Materials.—V., Metallic Compounds.—VI., The Manufacture of Mineral Pigments.—VII., The Manufacture of White Lead.—VIII., Enamel White.—IX., Washing Apparatus.—X., Zinc White.—XI., Yellow Mineral Pigments.—XII., Chrome Yellow.—XIII., Lead Oxide Pigments.—XIV., Other Yellow Pigments.—XV., Mosaic Gold.—XVI., Red Mineral Pigments.—XVII., The Manufacture of Vermilion.—XVIII., Antimony Vermilion.—XIX., Ferric Oxide Pigments.—XX., Other Red Mineral Pigments.—XXI., Purple of Cassius.—XXII., Blue Mineral Pigments.—XXIII., Ultramarine.—XXIV., Manufacture of Ultramarine.—XXV., Blue Copper Pigments.—XXVI., Blue Cobalt Pigments.—XXVII., Smalts.—XXVIII., Green Mineral Pigments.—XXIX., Emerald Green.—XXX., Verdigris.—XXXI., Chromium Oxide.—XXXII., Other Green Chromium Pigments.—XXXIII., Green Cobalt Pigments.—XXXIV., Green Manganese Pigments.—XXXV., Compounded Green Pigments.—XXXVI., Violet Mineral Pigments.—XXXVII., Brown Mineral Pigments.—XXXVIII., Brown Decomposition Products.—XXXIX., Black Pigments.—XL., Manufacture of Soot Pigments.—XLI., Manufacture of Lamp Black.—XLII., The Manufacture of Soot Black without Chambers.—XLIII., Indian Ink.—XLIV., Enamel Colours.—XLV., Metallic Pigments.—XLVI., Bronze Pigments—XLVII., Vegetable Bronze Pigments.

PIGMENTS OF ORGANIC ORIGIN.—Chapters XLVIII., Lakes.—XLIX., Yellow Lakes.—L., Red Lakes.—LI., Manufacture of Carmine.—LII., The Colouring Matter of Lac.—LIII., Safflower or Carthamine Red.—LIV., Madder and its Colouring Matters.—LV., Madder Lakes.—LVI., Manjit (Indian Madder).—LVII., Lichen Colouring Matters.—LVIII., Red Wood Lakes.—LIX., The Colouring Matters of Sandal Wood and Other Dye Woods.—LX., Blue Lakes.—LXI., Indigo Carmine.—LXII., The Colouring Matter of Log Wood.—LXIII., Green Lakes.—LXIV., Brown Organic Pigments.—LXV., Sap Colours.—LXVI., Water Colours.—LXVII., Crayons.—LXVIII., Confectionery Colours.—LXIX., The Preparation of Pigments for Painting.—LXX., The Examination of Pigments.—LXXI., Examination of Lakes.—LXXII., The Testing of Dye-Woods.—LXXIII., The Design of a Colour Works.—LXXIV.—Commercial Names of Pigments.—Appendix: Conversion of Metric to English Weights and Measures.—Centigrade and Fahrenheit Thermometer Scales.—Index.

BONE PRODUCTS AND MANURES: An Account of the most recent Improvements in the Manufacture of Fat, Glue, Animal Charcoal, Size, Gelatine and Manures. By THOMAS LAMBERT, Technical and Consulting Chemist. Illustrated by Twenty-one Plans and Diagrams. 162 pp., demy 8vo. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Chemical Composition of Bones—Arrangement of Factory—Crushing of Bones—Treatment with Benzene—Benzene in Crude Fat—Analyses of Clarified Fats—Mechanical Cleansing of Bones—Animal Charcoal—Tar and Ammoniacal Liquor, Char and Gases, from good quality Bones—Method of Retorting the Bones—Analyses of Chars—"Spent" Chars—Cooling of Tar and Ammoniacal Vapours—Value of Nitrogen for Cyanide of Potash—Bone Oil—Marrow Bones—Composition of Marrow Fat—Premier Juice—Buttons.—II., Properties of Glue—Glutin and Chondrin—Skin Glue—Liming of Skins—Washing—Boiling of Skins—Clarification of Glue Liquors—Acid Steeping of Bones—Water System of Boiling Bones—Steam Method of Treating Bones—Nitrogen in the Treated Bones—Glue-Boiling and Clarifying-House—Plan showing Arrangement of Clarifying Vats—Plan showing Position of Evaporators—Description of Evaporators—Sulphurous Acid Generator—Clarification of Liquors—Section of Drying-House—Specification of a Glue—Size—Uses and Preparation and Composition of Size—Concentrated Size.—III., Properties of Gelatine—Preparation of Skin Gelatine—Washing—Bleaching—Boiling—Clarification—Evaporation—Drying—Bone Gelatine—Selecting Bones—Crushing—Dissolving—Bleaching—Boiling—Properties of Glutin and Chondrin—Testing of Glues and Gelatines.—IV., The Uses of Glue, Gelatine and Size in Various Trades—Soluble and Liquid Glues—Steam and Waterproof Glues.—V., Manures—Importation of Food Stuffs—Soils—Germination—Plant Life.—VI., Natural Manures—Water and Nitrogen in Farmyard Manure—Full Analysis of Farmyard Manure—Action on Crops—Water-Closet

System—Sewage Manure—Green Manures.—VII., Artificial Manures—Bones—Boiled and Steamed Bones—Mineral Phosphates—English Coprolites—French and Spanish Phosphorites—German and Belgian Phosphates—Basic Slag—Guanos Proper—Guano Phosphates.—VIII., Mineral Manures—Common Salt—Potash Salts—Calcareous Manures—Prepared Nitrogenous Manures—Ammoniacal Compounds—Sodium Nitrate—Potassium Nitrate—Organic Nitrogenous Matters—Shoddy—Hoofs and Horns—Leather Waste—Dried Meat—Dried Blood—Superphosphates—Composition—Manufacture—Section of Manure-Shed—First and Ground Floor Plans of Manure-Shed—Quality of Acid Used—Mixings—Special Manures—Potato Manure—Dissolved Bones—Dissolved Bone Compound—Enriched Peruvian Guano—Special Manure for Garden Stuffs, etc.—Special Manure for Grass Lands—Special Tobacco Manures—Sugar-Cane Manure—Compounding of Manures—Valuation of Manures.—IX., Analyses of Raw and Finished Products—Common Raw Bones—Degreased Bones—Crude Fat—Refined Fat—Degelatinised Bones—Animal Charcoal—Bone Superphosphates—Guanos—Dried Animal Products—Potash Compounds—Sulphate of Ammonia—Extraction in Vacuo—Description of a Vacuum Pan—French and British Gelatines compared.—Index.

Press Opinion.

"We can with confidence recommend the perusal of the book to all persons interested in the manufacture of artificial manures, and also to the large number of farmers and others who are desirous of working their holdings on the most up-to-date methods, and obtaining the best possible results, which scientific research has placed within their reach."—*Wigan Observer.*

ANALYSIS OF RESINS AND BALSAMS. Demy 8vo. 340 pp. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Part I., Definition of Resins in General—Definition of Balsams, and especially the Gum Resins—External and Superficial Characteristics of Resinous Bodies—Distinction between Resinous Bodies and Fats and Oils—Origin, Occurrence and Collection of Resinous Substances—Classification—Chemical Constituents of Resinous Substances—Resinols—Resinot Annols—Behaviour of Resin Constituents towards the Cholesterine Reactions—Uses and Identification of Resins—Melting-point—Solvents—Acid Value—Saponification Value—Resin Value—Ester and Ether Values—Acetyl and Corbonyl Value—Methyl Value—Resin Acid—Systematic Résumé of the Performance of the Acid and Saponification Value Tests.

Part II., Balsams—Introduction—Definitions—Canada Balsam—Copaiba Balsam—Angostura Copaiba Balsam—Babia Copaiba Balsam—Carthagena Copaiba Balsam—Maracaibo Copaiba Balsam—Maturin Copaiba Balsam—Gurjum Copaiba Balsam—Para Copaiba Balsam—Surinam Copaiba Balsam—West African Copaiba Balsam—Mecca Balsam—Peruvian Balsam—Tolu Balsam—Acaroid Resin—Amine—Amber—African and West Indian Kino—Bengal Kino—Labdanum—Mastic—Pine Resin—Sandarach—Scammonium—Shellac—Storax—Adulteration of Styrax Liquidus Crudus—Purified Storax—Styrax Crudus Colatus—Tacamahac—Thapsia Resin—Turpentine—Chios Turpentine—Strassburg Turpentine—Turpeth Turpentine. **Gum Resins**—Ammoniacum—Bdellium—Euphorbium—Galbanum—Gamboge—Lactucarium—Myrrh—Opopanax—Sagapenum—Olibanum or Incense—Acaroid Resin—Amber—Thapsia Resin.—Index.

MANUFACTURE OF PAINT. A Practical Handbook for Paint Manufacturers, Merchants and Painters. By J. CRUICKSHANK SMITH, B.Sc. Demy 8vo. 1901. 200 pp. 60 Illustrations and 1 Large Diagram. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Part I., Chapters I., Preparation of Raw Material.—II., Storing of Raw Material.—III., Testing and Valuation of Raw Material—Paint Plant and Machinery.

Part II., Chapters V., The Grinding of White Lead.—VI., Grinding of White Zinc.—VII., Grinding of other White Pigments.—VIII., Grinding of Oxide Paints.—IX., Grinding of Staining Colours.—X., Grinding of Black Paints.—XI., Grinding of Chemical Colours—Yellows.—XII., Grinding of Chemical Colours—Blues.—XIII., Grinding Greens.—XIV., Grinding Reds.—XV., Grinding Lakes.—XVI., Grinding Colours in Water.—XVII., Grinding Colours in Turpentine.

Part III., Chapters XVIII., The Uses of Paint.—XIX., Testing and Matching Paints.—XX., Economic Considerations.—Index.

THE CHEMISTRY OF PIGMENTS. By ERNEST J. PARRY, B.Sc., F.I.C., F.C.S., and J. H. COSTE, F.I.C., F.C.S. [*In the press.*

Contents.

Chapters I., Introductory—Composition of White Light—Theory of Colour, etc.—II., The Application of Pigments—Artistic, Decorative, Protective Methods of Applying Pigments.—III., White Pigments.—IV., Inorganic Coloured Pigments.—V., Organic Pigments.

NOTES ON LEAD ORES: Their Distribution and Properties. By JAS. FAIRIE, F.G.S. Crown 8vo. 1901. 64 pages. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

Chapters I., Definitions—Properties—Occurrence.—II., Galena—Johnstonite—Cerussite—Céruse (White Lead)—Minium—Red Lead.—III., Pyromorphite—Mimetene—Hedyphane—Crocoise—Wulfenite.—Vanadinite—IV., Bleiglätte—Anglesite—Caledonite—Linarite—Lanarkite—Leadhillite — Susannite— Clausthalite — Cotunnite.—V., Mendipite — Matlockite — Cromfordite—Nagyagite—Altaite—Melanochroite — Vauquelinite — Scheeletine.—VI., Plattnerite—Tilkerodite—Raphanosmite—Deckenite—Descloezite—Dufrenaysite — Bleinierite — Moffrasite —Geocronite — Kilbrechenite — Schulzite—Boulangerite — Heteromorphite — Meneghinite—Jamesonite — Plagionite — Zinkenite.—VII., Kobellite — Bournonite— Selenkupferblei—Nussierite—Percylite—Wolchite—Polysphracrite—Miesite.—Index.

THE RISKS AND DANGERS OF VARIOUS OCCUPATIONS AND THEIR PREVENTION. By LEONARD A. PARRY, M.D., B.S. (Lond.). 196 pp., demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Occupations which are Accompanied by the Generation and Scattering of Abnormal Quantities of Dust.—II., Trades in which there is Danger of Metallic Poisoning.—III., Certain Chemical Trades.—IV., Some Miscellaneous Occupations.—V., Trades in which Various Poisonous Vapours are Inhaled.—VI., General Hygienic Considerations.—Index.

This book contains valuable information for the following trades—Aërated Water Manufacture, Alkali Manufacture, Aniline Manufacture, Barometer Making, Brass Founders, Bromine Manufacture, Bronze Moulders, Brush Making, Builders, Cabinet Makers, Calico Printing, Chloride of Lime Manufacture, Coal Miners, Cocoa-nut Fibre Making, Colour Grinders, Copper Miners, Cotton Goods Manufacture, Cotton Yarn Dyeing, Cutlery Trades, Dry Cleaning, Electricity Generating, Electroplaters, Explosives Manufacture, File Making, Flint Milling, Floor Cloth Makers, Furriers, Fustian Clothing Making, Galvanised Iron Manufacture, Gassing Process, Gilders, Glass Making, Glass Paper Making, Glass Polishing and Cutting, Grinding Processes, Gunpowder Manufacturing, Gutta-percha Manufacture, Hat Makers, Hemp Manufacture, Horn Goods Making, Horse-hair Making, Hydrochloric Acid Manufacture, India-rubber Manufacture, Iodine Manufacture, Ivory Goods Making, Jewellers, Jute Manufacture, Knife Grinders, Knife Handle Makers, Lace Makers, Lacquering, Lead Melters, Lead Miners, Leather Making, Linen Manufacture Linoleum Making, Lithographic Printing and Bronzing, Lithographing, Masons, Match Manufacture, Melanite Making, Mirror Making, Needle Grinders, Needle Making, Nitro-benzole Making, Nitro-glycerine Making, Paint Makers, Paper Making, Philosophical Instrument Makers, Photographers, Picric Acid Making, Portland Cement Making, Pottery Manufacture, Printers, Quicksilver Mining, Rag Pickers, Razor Grinders, Red Lead Making, Rope Making, Sand Paper Making, Saw Grinders, Scissors Grinders, Shoddy Manufacture, Shot Making, Silk Making, Silver Mining, Skinners, Slag, Wood Manufacture, Steel Makers, Steel Pen Making, Stereotypers, Stone Masons, Straw Hat Makers, Sulphuric Acid Manufacture, Sweeps, Table-knife Grinders, Tanners, Telegraphists, Textile Industries, Tin Miners, Turners, Type Founders, Umbrella Makers, Wall Paper Making, White Lead Making, Wood Working, Woollen Manufacture, Wool Sorters, Zinc Oxide Manufacture, Zinc Working, etc., etc.

Press Opinions.

"The language used is quite simple, and can be understood by any intelligent person engaged in the trades dealt with."—*The Clarion.*

"This is an appalling book. It shows that there is scarcely a trade or occupation that has not a risk or a danger attached to it."—*Local Government Journal.*

"Dr. Parry has not only pointed out the 'risks and dangers of various occupations'; he has suggested means for their prevention. The work is primarily a practical one."—*Colliery Manager.*

"This is a most useful book which should be in the hands of all employers of labour, foremen, and intelligent workmen, and is one of great utility to sanitary inspectors, and even on occasion to medical men."—*Health.*

"The writer has succeeded in collecting a large amount of information, and though one could wish he had presented it in a rather more attractive style, he has certainly condensed it into a very small space."—*Physician and Surgeon.*

"The little book before us is one which will be found exceedingly useful to manufacturers and even factory inspectors. . . . No attempt is made to show how diseases when originated are to be cured, but, acting on the sound principle that prevention is better than cure, means are stated how to avoid the harm."—*Bristol Mercury.*

"The author has endeavoured to treat the question in simple rather than in technical language, and he has lucidly catalogued the most dangerous trades and their symptoms, and in each case specified the best methods of dealing with them. . . . To those for whom the volume is specially designed, Dr. Parry's treatise should be a useful handbook."—*Sheffield Independent.*

"A very useful manual for employers of labour, foremen, intelligent workmen, and, in spite of the author's modesty, for medical men. We have the peculiar risks and dangers of all the dangerous trades carefully described; the mode of action of various chemicals, etc., used in different industries given, with full directions how to minimise unavoidable risks."—*Leeds Mercury.*

"Most of the trades in the country are alluded to, and upon those that are dangerous the necessary attention is bestowed, and means are recommended whereby danger may be prevented or lessened. The author has evidently studied his subject with care, and has made full use of the experience of others who have had a larger insight into the industries of the country."—*British Medical Journal.*

"The work is well written and printed, and its verbiage such as to be comprehensible to the workman no less than to the master. The careful and general perusal of a work of this nature cannot but be attended by beneficial results of a far-reaching nature, and we therefore heartily recommend the book to our readers. Medical Officers of Health and Sanitary Inspectors especially should find the work of great interest."—*Sanitary Record.*

"It is written in simple language, and its instructions can be easily followed. . . . There are some employers, at any rate, who are more ignorant of, than indifferent to, the slow murder of their workpeople, and if the facts so succinctly set forth in this book were brought to their notice, and if the Trade Unions made it their business to insist on the observance of the better conditions Dr. Parry described, much might be done to lessen the workman's peril."—*Weekly Times and Echo.*

PRACTICAL X RAY WORK. By FRANK T. ADDYMAN, B.Sc. (Lond.), F.I.C., Member of the Roentgen Society of London; Radiographer to St. George's Hospital; Demonstrator of Physics and Chemistry, and Teacher of Radiography in St. George's Hospital Medical School. Demy 8vo. 12 Plates from Photographs of X Ray Work. 52 Illustrations. 200 pp. 1901. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Part I., **Historical**—Chapters I., Introduction.—II., Work leading up to the Discovery of the X Rays.—III., The Discovery.

Part II., **Apparatus and its Management**—Chapters I., Electrical Terms.—II., Sources of Electricity.—III., Induction Coils.—IV., Electrostatic Machines.—V., Tubes.—VI., Air Pumps.—VII., Tube Holders and Stereoscopic Apparatus.—VIII., Fluorescent Screens.

Part III., **Practical X Ray Work**—Chapters I., Installations.—II., Radioscopy.—III., Radiography.—IV., X Rays in Dentistry.—V., X Rays in Chemistry.—VI., X Rays in War.—Index.

List of Plates.

Frontispiece—Congenital Dislocation of Hip-Joint.—I., Needle in Finger.—II., Needle in Foot.—III., Revolver Bullet in Calf and Leg.—IV., A Method of Localisation.—V., Stellate Fracture of Patella showing shadow of "Strapping".—VI., Sarcoma.—VII., Six-weeks'-old Injury to Elbow showing new Growth of Bone.—VIII., Old Fracture of Tibia and Fibula badly set.—IX., Heart Shadow.—X., Fractured Femur showing Grain of Splint.—XI., Barrell's Method of Localisation.

DRYING BY MEANS OF AIR AND STEAM. Explanations, Formulæ, and Tables for Use in Practice. Translated from the German of E. HAUSBRAND. Two Diagrams and Thirteen Tables. Demy 8vo. 1901. 72 pp. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Preface.—British and Metric Systems Compared—Centigrade and Fahr. Thermometers.—Chapters I., Introduction.—II., Estimation of the Maximum Weight of Saturated Aqueous Vapour which can be contained in 1 kilo. of Air at Different Pressure and Temperatures.—III., Calculation of the Necessary Weight and Volume of Air, and of the Least Expenditure of Heat, per Drying Apparatus with Heated Air, at the Atmospheric Pressure: *A*, With the Assumption that the Air is *Completely Saturated* with Vapour both before Entry and after Exit from the Apparatus.—*B*, When the Atmospheric Air is Completely Saturated *before entry*, but at its *exit* is *only* ¾, ½ or ¼ Saturated.—*C*, When the Atmospheric Air is *not* Saturated with Moisture before Entering the Drying Apparatus.—IV., Drying Apparatus, in which, in the Drying Chamber, a Pressure is Artificially Created, Higher or Lower than that of the Atmosphere.—V., Drying by Means of Superheated Steam, without Air.—VI., Heating Surface, Velocity of the Air Current, Dimensions of the Drying Room, Surface of the Drying Material, Losses of Heat.—Index.

Leather Trades.

THE LEATHER WORKER'S MANUAL. Being a Compendium of Practical Recipes and Working Formulæ for Curriers, Bootmakers, Leather Dressers, Blacking Manufacturers, Saddlers, Fancy Leather Workers, and all Persons engaged in the Manipulation of Leather. By H. C. STANDAGE. 165 pp. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Blackings, Polishes, Glosses, Dressings, Renovators, etc., for Boot and Shoe Leather.—II., Harness Blackings, Dressings, Greases, Compositions, Soaps, and Boot-top Powders and Liquids, etc., etc.—III., Leather Grinders' Sundries.—IV., Currier's Seasonings, Blacking Compounds, Dressings, Finishes, Glosses, etc.—V., Dyes and Stains for Leather.—VI., Miscellaneous Information.—VII., Chrome Tannage.—Index.

Press Opinions.

"The book being absolutely unique, is likely to be of exceptional value to all whom it concerns, as it meets a long-felt want."—*Birmingham Gazette.*

"This is a valuable collection of practical receipts and working formulæ for the use of those engaged in the manipulation of leather. We have no hesitation in recommending it as one of the best books of its kind, an opinion which will be endorsed by those to whom it appeals."—*Liverpool Mercury.*

"We think we may venture to state, so far as the opinion of the leather trade under the Southern Cross is concerned, that it will be one of approval. As practical men, having a long and wide experience of the leather trade in Australia, we are certain that there are many tanners and curriers carrying on business in remote townships of the colonies to whom such a manual of practical recipes will be invaluable. . . . This manual is not a mere collection of recipes for the various purposes to which they may be applied, but it is also replete with instructions concerning the nature of the materials recommended to be used in making up the recipes. . . . We think every intelligent leather man should avail himself of the manual. It is undoubtedly a valuable contribution to the technology of the leather trade."—*Australian Leather Journal and Boot and Shoe Recorder.*

PRACTICAL TREATISE ON THE LEATHER INDUSTRY. By A. M. VILLON. A Translation of Villon's "Traité Pratique de la Fabrication des cuirs et du Travail des Peaux". By FRANK T. ADDYMAN, B.Sc. (Lond.), F.I.C., F.C.S.; and Corrected by an Eminent Member of the Trade. 500 pp., royal 8vo. 1901. 123 Illustrations. Price 21s.; India and Colonies, 22s.; Other Countries, 23s. 6d.; strictly net.

Contents.

Preface—Translator's Preface—List of Illustrations.

Part I., **Materials used in Tanning**—Chapter I., Skins: I., Skin and its Structure; II., Skins used in Tanning; III., Various Skins and their Uses—Chapter II., Tannin and Tanning Substances: I., Tannin; II., Barks (Oak); III., Barks other than Oak; IV., Tanning Woods; V., Tannin-bearing Leaves; VI., Excrescences; VII., Tan-bearing Fruits; VIII., Tan-bearing Roots and Bulbs; IX., Tanning Juices; X., Tanning Substances used in Various Countries; XI., Tannin Extracts; XII., Estimation of Tannin and Tannin Principles.

Part II., **Tanning**—Chapter I., The Installation of a Tannary: I., Tan Furnaces; II., Chimneys, Boilers, etc.; III., Steam Engines—Chapter II., Grinding and Trituration of Tanning Substances: I., Cutting up Bark; II., Grinding Bark; III., The Grinding of Tan Woods; IV., Powdering Fruit, Galls and Grains; V., Notes on the Grinding of Bark—Chapter III., Manufacture of Sole Leather: I., Soaking; II., Sweating and Unhairing; III., Plumping and Colouring; IV., Handling; V., Tanning; VI., Tanning Elephants' Hides; VII., Drying; VIII., Striking or Pinning—Chapter IV., Manufacture of Dressing Leather: I., Soaking; II., Depilation; III., New Processes for the Depilation of Skins; IV., Tanning; V., Cow Hides; VI., Horse Hides; VII., Goat Skins; Manufacture of Split Hides—Chapter V., On Various Methods of Tanning: I., Mechanical Methods; II., Physical Methods; III., Chemical Methods; IV., Tanning with Extracts—Chapter VI., Quantity and Quality: I., Quantity; II., Net Cost; III., Quality of Leather—Chapter VII., Various Manipulations of Tanned Leather: I., Second Tanning; II., Grease Stains; III., Bleaching Leather; IV., Waterproofing Leather; V., Weighting Tanned Leather; VI., Preservation of Leather—Chapter VIII., Tanning Various Skins.

Part III., **Currying**—Chapter I., Waxed Calf: I., Preparation; II., Shaving; III., Stretching or Slicking; IV., Oiling the Grain; V., Oiling the Flesh Side; VI., Whitening and Graining; VII., Waxing; VIII., Finishing; IX., Dry Finishing; X., Finishing in Colour; XI., Cost—Chapter II., White Calf: I., Finishing in White—Chapter III., Cow Hide for Upper Leathers: I., Black Cow Hide; II., White Cow Hide; III., Coloured Cow Hide.—Chapter IV., Smooth Cow Hide—Chapter V., Black Leather—Chapter VI., Miscellaneous Hides: I., Horse; II., Goat; III., Waxed Goat Skin; IV., Matt Goat Skin—Chapter VII., Russia Leather: I., Russia Leather; II.. Artificial Russia Leather.

Part IV., **Enamelled, Hungary and Chamoy Leather, Morocco, Parchment, Furs and Artificial Leather**—Chapter I., Enamelled Leather: I., Varnish Manufacture; II., Application of the Enamel; III., Enamelling in Colour—Chapter II., Hungary Leather: I., Preliminary; II., Wet Work or Preparation; III., Aluming; IV., Dressing or Loft Work; V., Tallowing; VI., Hungary Leather from Various Hides—Chapter III., Tawing: I., Preparatory Operations; II., Dressing; III., Dyeing Tawed Skins; IV., Rugs—Chapter IV., Chamoy Leather—Chapter V., Morocco: I., Preliminary Operations; II., Morocco Tanning; III., Mordants used in Morocco Manufacture; IV., Natural Colours used in Morocco Dyeing; V., Artificial Colours; VI. Different Methods of Dyeing; VII., Dyeing with Natural Colours; VIII., Dyeing with Aniline Colours; IX., Dyeing with Metallic Salts; X., Leather Printing; XI., Finishing Morocco; XII., Shagreen; XIII., Bronzed Leather—Chapter VI., Gilding and Silvering: I., Gilding; II., Silvering; III., Nickel and Cobalt—Chapter VII., Parchment—Chapter VIII., Furs and Furriery: I., Preliminary Remarks; II., Indigenous Furs; III., Foreign Furs from Hot Countries; IV. Foreign Furs from Cold Countries; V., Furs from Birds' Skins; VI., Preparation of Furs; VII., Dressing; VIII., Colouring; IX., Preparation of Birds' Skins; X., Preservation of Furs—Chapter IX., Artificial Leather: I., Leather made from Scraps; II., Compressed Leather; III., American Cloth; IV., Papier Mâché; V., Linoleum; VI., Artificial Leather.

Part V., **Leather Testing and the Theory of Tanning**—Chapter I., Testing and Analysis of Leather: I., Physical Testing of Tanned Leather; II., Chemical Analysis—Chapter II., The Theory of Tanning and the other Operations of the Leather and Skin Industry: I., Theory of Soaking; II., Theory of Unhairing; III., Theory of Swelling; IV., Theory of Handling; V. Theory of Tanning; VI., Theory of the Action of Tannin on the Skin; VII., Theory of Hungary Leather Making; VIII., Theory of Tawing; IX., Theory of Chamoy Leather Making; X., Theory of Mineral Tanning.

Part VI., **Uses of Leather**—Chapter I., Machine Belts: I., Manufacture of Belting; II., Leather Chain Belts; III., Various Belts, IV., Use of Belts—Chapter II., Boot and Shoemaking: I., Boots and Shoes; II., Laces—Chapter III., Saddlery: I., Composition of a Saddle; II., Construction of a Saddle—Chapter IV., Harness: I., The Pack Saddle; II., Harness—Chapter V., Military Equipment—Chapter VI., Glove Making—Chapter VII., Carriage Building—Chapter VIII., Mechanical Uses.

Appendix, **The World's Commerce in Leather**—I., Europe; II., America; III., Asia; IV., Africa; Australasia—Index.

Press Opinions.

"The book is well and lucidly written. The writer is evidently a practical man, who also has taken the trouble to make himself acquainted with the scientific and technical side of his trade. . . . French methods differ largely from our own; sometimes we think our ways the best, but not always. The practical man may pick up many useful hints which may help him to improve his methods."—*Shoe Manufacturers' Monthly Journal.*

"This book cannot fail to be of great value to all engaged in the leather trades. . . . The British may believe that the French can teach them nothing in the work of leather tanning generally, but a comparison of the methods of the two countries will certainly yield a few wrinkles which may lead to advantageous results. Only a man understanding the science and technique of the trade could have written the book, and it is well done."—*Midland Free Press.*

"Gives much useful and interesting information concerning the various processes by which the skins of animals are converted into leather. Written by a French Chemist after five years of constant study and application; it shows all that detail of analysis which we are accustomed to find in scientists, and which the practical tanner is too much in the habit of ignoring, sometimes to his own loss."—*Leeds Mercury.*

"Nor can there be much doubt that this expectation will be fully justified by the result. Thanks to the conspicuous painstaking with which Mr. Addyman has discharged his duty, and the 123 illustrations by which the text is elucidated, the volume can hardly fail to prove a very valuable standard work of its class. It can thus be confidently recommended to all who are more or less practically interested in the technology of a very important subject."—*Leicester Post.*

"This is, in every respect, an altogether admirable, practical, clear and lucid treatise on the various and numerous branches of the great leather industry, of which it deals in an exhaustive, highly intelligent, workmanlike and scientific manner. . . . It is a handsome addition to every man's knowledge of his trade, whether he be a leading director of a large public company, or an industrious employee in the works, wishing to improve his services by the addition of his brains to his work."—*Shoe and Leather Trader.*

"M. Villon writes as one having a very full knowledge of all branches of the subject, and in days when foreign competition has enforced on English manufacturers the importance of no longer being content with rule-of-thumb methods which have come down to them from their forefathers it certainly should be worth the while of English tanners to see what lessons they can learn from French practice, and French practice, we should imagine, could hardly have a better exponent than the author of this large volume."—*Western Daily Press and Bristol Times.*

"At a time when all or nearly all our British industries are to a greater or less extent hampered by the pressure of continental and American competition, any hints that can be obtained as to the methods pursued by competitors must necessarily be of value. . . . That it will be of interest and value, not merely to English tanners, but to those associated with many kindred industrial branches, goes without saying. . . . As a work of reference the volume will be extremely useful in the trade, and where leisure affords sufficient opportunity a careful perusal and study of it would afford ample reward."—*Kettering Guardian.*

"This is a very handsomely got up and elaborate work just issued by this well-known technical book-publishing firm. . . . When we say that the work consists of over 500 large pages with about 120 illustrations, and almost innumerable tables, it will be seen at once that

we cannot attempt anything like an exhaustive *résumé* of its contents, and even if we did the details would be of little interest to our general readers, while those who are engaged in the leather industry will probably obtain the book for themselves—at least they would do well to do so. . . . Altogether the 'Treatise' has evidently been very carefully prepared, and by a man who thoroughly knows the subject, and hence it will be a very valuable technical book for English firms and workers."—*Walsall Observer.*

Books on Pottery, Bricks, Tiles, Glass, etc.

THE MANUAL OF PRACTICAL POTTING. Revised and Enlarged. Third Edition. 200 pp. 1901. Price 17s. 6d.; India and Colonies, 18s. 6d.; Other Countries, 20s. ; strictly net.

Contents.

Introduction. The Rise and Progress of the Potter's Art.—Chapters I., **Bodies.** China and Porcelain Bodies, Parian Bodies, Semi-porcelain and Vitreous Bodies, Mortar Bodies, Earthenwares Granite and C.C. Bodies, Miscellaneous Bodies, Sagger and Crucible Clays, Coloured Bodies, Jasper Bodies, Coloured Bodies for Mosaic Painting, Encaustic Tile Bodies, Body Stains, Coloured Dips.—II., **Glazes.** China Glazes, Ironstone Glazes, Earthenware Glazes, Glazes without Lead, Miscellaneous Glazes, Coloured Glazes, Majolica Colours.—III., **Gold and Cold Colours.** Gold, Purple of Cassius, Marone and Ruby, Enamel Coloured Bases, Enamel Colour Fluxes, Enamel Colours, Mixed Enamel Colours, Antique and Vellum Enamel Colours, Underglaze Colours, Underglaze Colour Fluxes, Mixed Underglaze Colours, Flow Powders, Oils and Varnishes.—IV., **Means and Methods.** Reclamation of Waste Gold, The Use of Cobalt, Notes on Enamel Colours, Liquid or Bright Gold.—V., **Classification and Analysis.** Classification of Clay Ware, Lord Playfair's Analysis of Clays, The Markets of the World, Time and Scale of Firing, Weights of Potter's Material, Decorated Goods Count.—VI., Comparative Loss of Weight of Clays.—VII., Ground Felspar Calculations.—VIII., The Conversion of Slop Body Recipes into Dry Weight.—IX., The Cost of Prepared Earthenware Clay.—X., **Forms and Tables.** Articles of Apprenticeship, Manufacturer's Guide to Stocktaking, Table of Relative Values of Potter's Materials, Hourly Wages Table, Workman's Settling Table, Comparative Guide for Earthenware and China Manufacturers in the use of Slop Flint and Slop Stone, Foreign Terms applied to Earthenware and China Goods, Table for the Conversion of Metrical Weights and Measures on the Continent of South America. **Index.**

CERAMIC TECHNOLOGY: Being some Aspects of Technical Science as Applied to Pottery Manufacture. Edited by CHARLES F. BINNS. 100 pp. 1897. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

Preface.—Introduction.—Chapters I., The Chemistry of Pottery.—II., Analysis and Synthesis.—III., Clays and their Components.—IV., The Biscuit Oven.—V., Pyrometry.—VI., Glazes and their Composition.—VII., Colours and Colour-making.—Index.

RECIPES FOR FLINT GLASS MAKING. By a British Glass Master and Mixer. Sixty Recipes. Being Leaves from the Mixing Book of several experts in the Flint Glass Trade, containing up-to-date recipes and valuable information as to Crystal, Demi-crystal and Coloured Glass in its many varieties. It contains the recipes for cheap metal suited to pressing, blowing, etc., as well as the most costly crystal and ruby. British manufacturers have kept up the quality of this glass from the arrivals of the Venetians to Hungry Hill, Stourbridge, up to the present time. The book also contains remarks as to the result of the metal as it left the pots by the respective metal mixers, taken from their own memoranda upon the originals. 1900. Price for United Kingdom, 10s. 6d.; Abroad. 15s.; United States, $4; strictly net.

Contents.

Ruby—Ruby from Copper—Flint for using with the Ruby for Coating—A German Metal—Cornelian, or Alabaster—Sapphire Blue—Crysophis—Opal—Turquoise Blue—Gold Colour—Dark Green—Green (common)—Green for Malachite—Blue for Malachite—Black for Malachite—Black—Common Canary Batch—Canary—White Opaque Glass—Sealing-wax Red—Flint—Flint Glass (Crystal and Demi)—Achromatic Glass—Paste Glass—White Enamel—Firestone—Dead White (for moons)—White Agate—Canary—Canary Enamel—Index.

COLOURING AND DECORATION OF CERAMIC WARE. By ALEX. BRONGNIART. With Notes and Additions by ALPHONSE SALVETAT. Translated from the French. 200 pp. 1898. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

The Pastes, Bodies or Ceramic Articles Capable of being Decorated by Vitrifiable Colours —The Chemical Preparation of Vitrifiable Colours—Composition and Preparation of Vitrifiable Colours—The Oxides—Preparation of Oxides—Preparation of Chromates—Preparation of other Colours—Composition and Preparation of Fluxes—Muffle Colours—Recipes for Colours —Use of Metals—Lustres—Preparation and Application of Colours—Composition of Coloured Pastes—Underglaze Colours—Colours in the Glaze—Overglaze Colours—Painting in Vitrifiable Colours—Gilding—Burnishing—Printing—Enlarging and Reducing Gelatine Prints—Muffle Kilns for Vitrifiable Colours—Influence of the Material on the Colour—Changes Resulting from the Actions of the Fire—Alterations Resulting from the Colours—Alterations in Firing.

HOW TO ANALYSE CLAY. Practical Methods for Practical Men. By HOLDEN M. ASHBY, Professor of Organic Chemistry, Harvey Medical College, U.S.A. Twenty Illustrations. 1898. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

List of Apparatus—List of Atomic Weights—Use of Balance, and Burette, Sand Bath, and Water Bath—Dessicator—Drying Oven—Filtering—Fusion—Determination of Water, Organic Matter, Iron, Calcium, Alkalies, Limestone, Silica, Alumina, Magnesium, etc.—Mechanical Analysis—Rational Analysis—Standard Solutions—Volumetric Analysis—Standards for Clay Analysis—Sampling.

ARCHITECTURAL POTTERY. Bricks, Tiles, Pipes, Enamelled Terra-cottas, Ordinary and Incrusted Quarries, Stoneware Mosaics, Faïences and Architectural Stoneware. By LEON LEFÈVRE. With Five Plates. 950 Illustrations in the Text, and numerous estimates. 500 pp., royal 8vo. 1900. Translated from the French by K. H. BIRD, M.A., and W. MOORE BINNS. Price 15s.; India and Colonies, 16s.; Other Countries, 17s. 6d.; strictly net.

Contents.

Part I. **Plain Undecorated Pottery.**—Chapter I., Clays: § 1, Classification, General Geological Remarks.—Classification, Origin, Locality; § 2, General Properties and Composition: Physical Properties, Contraction, Analysis, Influence of Various Substances on the Properties of Clays; § 3, Working of Clay-Pits—I. Open Pits: Extraction, Transport, Cost—II. Underground Pits—Mining Laws. Chapter II., Preparation of the Clay: Weathering, Mixing, Cleaning, Crushing and Pulverising—Crushing Cylinders and Mills, Pounding Machines—Damping: Damping Machines—Soaking, Shortening, Pugging: Horse and Steam Pug-Mills, Rolling Cylinders—Particulars of the Above Machines. Chapter III., Bricks: § 1, Manufacture —(1) Hand and Machine Moulding.—I. Machines Working by Compression: on Soft Clay, on Semi-Firm Clay, on Firm Clay, on Dry Clay.—II. Expression Machines: with Cylindrical Propellers, with Screw Propellers—Dies—Cutting-tables—Particulars of the Above Machines—General Remarks on the Choice of Machines—Types of Installations—Estimates—Plenishing, Hand and Steam Presses, Particulars—(2) Drying, by Exposure to Air, Without Shelter, and Under Sheds—Drying-rooms in Tiers, Closed Drying-rooms, in Tunnels, in Galleries—Detailed Estimates of the Various Drying-rooms, Comparison of Prices—Transport from the Machines to the Drying-rooms, Barrows, Trucks, Plain or with Shelves, Lifts—(3) Firing —I. In Clamps—II. In Intermittent Kilns. *A*, Open: *a*, using Wood; *b* Coal; *b'*, in Clamps; *b''*, Flame—*B*, Closed: *c*, Direct Flame; *c'*, Rectangular; *c''*, Round; *d*, Reverberatory—III. Continuous Kilns: *C*, with Solid Fuel: Round Kiln, Rectangular Kiln, Chimneys (Plans and Estimates)—*D*, With Gas Fuel, Fillard Kiln (Plans and Estimates), Schneider Kiln (Plans and Estimates), Water-gas Kiln—Heat Production of the Kilns; § 2, Dimensions, Shapes, Colours, Decoration, and Quality of Bricks—Hollow Bricks, Dimensions and Prices of Bricks, Various Shapes, Qualities—Various Hollow Bricks, Dimensions, Resistance, Qualities; § 3, Applications —History—Asia, Africa, America, Europe: Greek, Roman, Byzantine, Turkish, Romanesque, Gothic, Renaissance, Architecture—Architecture of the Nineteenth Century: in Germany, England, Belgium, Spain, Holland, France, America—Use of Bricks—Walls, Arches, Pavements, Flues, Cornices—Facing with Coloured Bricks—Balustrades. Chapter IV., Tiles: § 1, History; § 2, Manufacture—(1) Moulding, by Hand, by Machinery: Preparation of the Clay, Soft Paste, Firm Paste, Hard Paste—Preparation of the Slabs, Transformation into Flat Tiles, into Jointed Tiles—Screw, Cam and Revolver Presses—Particulars of Tile-presses—(2) Drying—Planchettes, Shelves, Drying-barrows and Trucks—(3) Firing—Divided Kilns—Installation of Mechanical Tileworks—Estimates; § 3, Shapes, Dimensions and Uses of the Principal Types of Tile—Ancient Tiles: Flat, Round, Roman, Flemish—Modern Tiles—With Vertical Interrupted Join: Gilardoni's, Martin's; Hooked, Boulet's Villa; with Vertical Continuous Join: Muller's, Alsace, Pantile—Foreign Tiles—Special Tiles—Ridge Tiles, Coping Tiles, Border Tiles, Frontons, Gutters, Antefixes, Membron, Angular—Roofing Accessories: Chimney-pots,

Mitrons, Lanterns, Chimneys—Qualities of Tiles—Black Tiles—Stoneware Tiles—Particulars of Tiles. Chapter V., Pipes: I. Conduit Pipes—Manufacture—Moulding: Horizontal Machines, Vertical Machines, Worked by Hand and Steam—Particulars of these Machines—Drying—Firing—II. Chimney Flues—Ventiducts and "Boisseaux," "Waggons"—Particulars of these Products. Chapter VI., Quarries: 1, Plain Quarries of Ordinary Clay; 2, of Cleaned Clay—Machines, Cutting, Mixing, Polishing—Drying and Firing—Applications—Particulars of Quarries. Chapter VII., Terra-cotta: History—Manufacture—Application: Balustrades, Columns, Pilasters, Capitals, Friezes, Frontons, Medallions, Panels, Rose-windows, Ceilings—Appendix: Official Methods of Testing Terra-cottas.

Part II. **Made-up or Decorated Pottery.**—Chapter I., General Remarks on the Decoration of Pottery: Dips—Glazes: Composition, Colouring, Preparation, Harmony with Pastes—Special Processes of Decoration—Enamels, Opaque, Transparent, Colours, Underglaze, Over-glaze—Other Processes: Crackling, Mottled, Flashing, Metallic Iridescence, Lustres. Chapter II., Glazed and Enamelled Bricks—History: Glazing—Enamelling—Applications: Ordinary Enamelled Bricks, Glazed Stoneware, Enamelled Stoneware—Enamelled Tiles. Chapter III., Decorated Quarries: I. Paving Quarries—1, Decorated with Dips—2, Stoneware: *A*, Fired to Stoneware; *a*, of Slag Base—Applications; *b*, of Melting Clay—Applications—*B*, Plain or Incrusted Stoneware; *a*, of Special Clay (Stoke-on-Trent)—Manufacture—Application—*b*, of Felspar Base—Colouring, Manufacture, Moulding, Drying, Firing—Applications.—II. Facing Quarries—1, in Faïence—*A*, of Limestone Paste—*B*, of Silicious Paste—*C*, of Felspar Paste—Manufacture, Firing—2, of Glazed Stoneware—3, of Porcelain—Applications of Facing Quarries.—III. Stove Quarries—Preparation of the Pastes, Moulding, Firing, Enamelling, Decoration—Applications—Faïences for Fireplaces. Chapter IV., Architectural Decorated Pottery: § 1, Faïences; § 2, Stoneware; § 3, Porcelain. Chapter V., Sanitary Pottery: Stoneware Pipes: Manufacture, Firing—Applications—Sinks—Applications—Urinals, Seats and Pans—Applications—Drinking-fountains, Washstands. Index.

A TREATISE ON THE CERAMIC INDUSTRIES.

A Complete Manual for Pottery, Tile and Brick Works. By EMILE BOURRY, Ingénieur des Arts et Manufactures. Translated from the French by WILTON P. RIX, Examiner in Pottery and Porcelain to the City and Guilds of London Technical Institute, Pottery Instructor to the Hanley School Board. Royal 8vo. 1901. Over 700 pp. Price 21s.; India and Colonies, 22s.; Other Countries, 23s. 6d.; strictly net.

Contents.

Part I., **General Pottery Methods.** Chapters I., Definition and History. Definitions and Classification of Ceramic Products—Historic Summary of the Ceramic Art.—II., Raw Materials of Bodies. Clays: Pure Clay and Natural Clays—Various Raw Materials: Analogous to Clay—Agglomerative and Agglutinative—Opening—Fusible—Refractory—Trials of Raw Materials.—III., Plastic Bodies. Properties and Composition—Preparation of Raw Materials: Disaggregation—Purification—Preparation of Bodies: By Plastic Method—By Dry Method—By Liquid Method.—IV., Formation. Processes of Formation: Throwing—Expression—Moulding by Hand, on the Jolley, by Compression, by Slip Casting—Slapping—Slipping.—V., Drying. Drying of Bodies—Processes of Drying: By Evaporation—By Aeration—By Heating—By Ventilation—By Absorption.—VI., Glazes. Composition and Properties—Raw Materials—Manufacture and Application.—VII., Firing. Properties of the Bodies and Glazes during Firing—Description of the Kilns—Working of the Kilns.—VIII., Decoration. Colouring Materials—Processes of Decoration.

Part II., **Special Pottery Methods.** Chapters IX., Terra Cottas. Classification: Plain Ordinary, Hollow, Ornamental, Vitrified, and Light Bricks—Ordinary and Black Tiles—Paving Tiles—Pipes—Architectural Terra Cottas—Vases, Statues and Decorative Objects—Common Pottery—Pottery for Water and Filters—Tobacco Pipes—Lustre Ware—Properties and Tests for Terra Cottas.—X., Fireclay Goods. Classification: Argillaceous, Aluminous, Carboniferous, Silicious and Basic Fireclay Goods—Fireclay Mortar (Pug)—Tests for Fireclay Goods.—XI., Faiences. Varnished Faiences—Enamelled Faiences—Silicious Faiences—Pipe-clay Faiences—Pebble Work—Feldspathic Faiences—Composition, Processes of Manufacture and General Arrangements of Faience Potteries.—XII., Stoneware. Stoneware Properly So-called: Paving Tiles—Pipes—Sanitary Ware—Stoneware for Food Purposes and Chemical Productions—Architectural Stoneware—Vases, Statues and other Decorative Objects—Fine Stoneware.—XIII., Porcelain. Hard Porcelain for Table Ware and Decoration, for the Fire, for Electrical Conduits, for Mechanical Purposes; Architectural Porcelain, and Dull or Biscuit Porcelain—Soft Phosphated or English Porcelain—Soft Vitreous Porcelain, French and New Sèvres—Argillaceous Soft or Seger's Porcelain—Dull Soft or Parian Porcelain—Dull Feldspathic Soft Porcelain.—**Index.**

THE ART OF RIVETING GLASS, CHINA AND EARTHENWARE.

By J. HOWARTH. Second Edition. 1900. Price 1s. net; by post, home or abroad, 1s. 1d.

Contents.

Tools and Materials Required—Wire Used for Rivets—Soldering Solution—Preparation for Drilling—Commencement of Drilling—Cementing—Preliminaries to Riveting—Rivets to Make—To Fix the Rivets—Through-and-through Rivets—Soldering—Tinning a Soldering-Iron—Perforated Plates, Handles, etc.—Handles of Ewers, etc.—Vases and Comports—Marble and Alabaster Ware—Decorating—How to Loosen Fast Decanter Stoppers—China Cements.

NOTES OF POTTERY CLAYS. Their Distribution, Properties, Uses and Analyses of Ball Clays, China Clays and China Stone. By JAS. FAIRIE, F.G.S. 1901. 132 pp. Crown 8vo. Price 3s. 6d.; India and Colonies, 4s.; Other Countries, 4s. 6d.; strictly net.

Contents.

Definitions—Occurrence—Brick Clays—Fire Clays—Analyses of Fire Clays.—**Ball Clays**—Properties—Analyses—Occurrence—Pipe Clay—Black Clay—Brown Clay—Blue Clay—Dorsetshire and Devonshire Clays.—**China Clay** or Kaolin—Occurrence—Chinese Kaolin—Cornish Clays—Hensbarrow Granite—Properties, Analyses and Composition of China Clays—Method of Obtaining China Clay—Experiments with Chinese Kaolin—Analyses of Chinese and Japanese Clays and Bodies—Irish Clays.—**Chinese Stone**—Composition—Occurrence—Analyses.—Index.

PAINTING ON GLASS AND PORCELAIN AND ENAMEL PAINTING. A Complete Introduction to the Preparation of all the Colours and Fluxes used for Painting on Porcelain, Enamel, Faïence and Stoneware, the Coloured Pastes and Coloured Glasses, together with a Minute Description of the Firing of Colours and Enamels. On the Basis of Personal Practical Experience of the Condition of the Art up to Date. By FELIX HERMANN, Technical Chemist. With Eighteen Illustrations. 300 pp. Translated from the German second and enlarged Edition. 1897. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

History of Glass Painting.—Chapters I., The Articles to be Painted: Glass, Porcelain, Enamel, Stoneware, Faïence.—II., Pigments: 1, Metallic Pigments: Antimony Oxide, Naples Yellow, Barium Chromate, Lead Chromate, Silver Chloride, Chromic Oxide.—III., Fluxes: Fluxes, Felspar, Quartz, Purifying Quartz, Sedimentation, Quenching, Borax, Boracic Acid, Potassium and Sodium Carbonates, Rocaille Flux.—IV., Preparation of the Colours for Glass Painting.—V., The Colour Pastes.—VI., The Coloured Glasses.—VII., Composition of the Porcelain Colours.—VIII., The Enamel Colours: Enamels for Artistic Work.—IX., Metallic Ornamentation: Porcelain Gilding, Glass Gilding.—X., Firing the Colours: 1, Remarks on Firing: Firing Colours on Glass, Firing Colours on Porcelain; 2, The Muffle.—XI., Accidents occasionally Supervening during the Process of Firing.—XII., Remarks on the Different Methods of Painting on Glass, Porcelain, etc.—Appendix: Cleaning Old Glass Paintings.

Press Opinions.

"Mr. Hermann, by a careful division of his subject, avoids much repetition, yet makes sufficiently clear what is necessary to be known in each art. He gives very many formulæ; and his hints on the various applications of metals and metallic lustres to glass and porcelains will be found of much interest to the amateur."—*Art Amateur*, New York.

"For the unskilled and amateurs the name of the publishers will be sufficient guarantee for the utility and excellence of Mr. Hermann's work, even if they are already unacquainted with the author. . . . The whole cannot fail to be both of service and interest to glass workers and to potters generally, especially those employed upon high-class work."—*Staffordshire Sentinel.*

"In *Painting on Glass and Porcelain* the author has dealt very exhaustively with the technical as distinguished from the artistic side of his subject, the work being entirely devoted to the preparation of the colours, their application and firing. For manufacturers and students it will be a valuable work, and the recipes which appear on almost every page form a very valuable feature. The author has gained much of his experience in the celebrated Sevres manufactory, a fact which adds a good deal of authority to the work."—*Builders Journal.*

"The compiler displays that painstaking research characteristic of his nation, and goes at length into the question of the chemical constitution of the pigments and fluxes to be used in glass-painting, proceeding afterwards to a description of the methods of producing coloured glass of all tints and shades. . . . Very careful instructions are given for the chemical and mechanical preparation of the colours used in glass-staining and porcelain-painting; indeed, to the china painter such a book as this should be of permanent value, as the author claims to have tested and verified every recipe he includes, and the volume also comprises a section devoted to enamels both opaque and translucent, and another treating of the firing of porcelain, and the accidents that occasionally supervene in the furnace."—*Daily Chronicle.*

A Reissue of

THE HISTORY OF THE STAFFORDSHIRE POTTERIES; AND THE RISE AND PROGRESS OF THE MANUFACTURE OF POTTERY AND PORCELAIN. With References to Genuine Specimens, and Notices of Eminent Potters. By SIMEON SHAW. (Originally Published in 1829.) 265 pp. 1900. Demy 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Introductory Chapter showing the position of the Pottery Trade at the present time 1899).—Chapters I., **Preliminary Remarks.**—II., **The Potteries**, comprising Tunstall, Brownhills, Greenfield and New Field, Golden Hill, Latebrook, Green Lane, Burslem, Longport and Dale Hall, Hot Lane and Cobridge, Hanley and Shelton, Etruria, Stoke, Penkhull, Fenton, Lane Delph, Foley, Lane End.—III., **On the Origin of the Art,** and its Practice among the early Nations.—IV., **Manufacture of Pottery,** prior to 1700.—V., **The Introduction of Red Porcelain** by Messrs. Elers, of Bradwell, 1690.—VI., **Progress of the Manuacture** from 1700 to Mr. Wedgwood's commencement in 1760.—VII. **Introduction of Fluid Glaze.**—Extension of the Manufacture of Cream Colour.—Mr. Wedgwood's Queen's Ware.—Jasper, and Appointment of Potter to Her Majesty.—Black Printing.—VIII., **Introduction of Porcelain.** Mr. W. Littler's Porcelain.—Mr. Cookworthy's Discovery of Kaolin and Petuntse, and Patent.—Sold to Mr. Champion—resold to the New Hall Com.—Extension of Term.—IX., **Blue Printed Pottery.** Mr. Turner, Mr. Spode (1), Mr. Baddeley, Mr. Spode (2), Messrs. Turner, Mr. Wood, Mr. Wilson, Mr. Minton.—Great Change in Patterns of Blue Printed.—X., **Introduction of Lustre Pottery.** Improvements in Pottery and Porcelain subsequent to 1800.

Press Opinions.

"There is much curious and useful information in the work, and the publishers have rendered the public a service in reissuing it."—*Burton Mail.*

"Copies of the original work are now of considerable value, and the facsimile reprint now issued cannot but prove of considerable interest to all interested in the great industry."—*Derby Mercury.*

"The book will be especially welcomed at a time when interest in the art of pottery manufacture commands a more widespread and general interest than at any previous time."—*Wolverhampton Chronicle.*

"This work is all the more valuable because it gives one an idea of the condition of affairs existing in the north of Staffordshire before the great increase in work and population due to modern developments."—*Western Morning News.*

. . The History gives a graphic picture of North Staffordshire at the end of the last and the beginning of the present century, and states that in 1829 there was 'a busy and enterprising community' in the Potteries of fifty thousand persons. . . . We commend it to our readers as a most entertaining and instructive publication."—*Staffordshire Sentinel.*

A Reissue of

THE CHEMISTRY OF THE SEVERAL NATURAL AND ARTIFICIAL HETEROGENEOUS COMPOUNDS USED IN MANUFACTURING PORCELAIN, GLASS AND POTTERY.

By SIMEON SHAW. (Originally published in 1837.) 750 pp. 1900. Royal 8vo. Price 14s.; India and Colonies, 15s.; Other Countries, 16s. 6d.; strictly net.

Contents.

PART I., ANALYSIS AND MATERIALS.—Chapters I., **Introduction:** Laboratory and Apparatus; **Elements:** Combinative Potencies, Manipulative Processes for Analysis and Reagents, Pulverisation, Blow-pipe Analysis, Humid Analysis, Preparatory Manipulations, General Analytic Processes, Compounds Soluble in Water, Compounds Soluble only in Acids, Compounds (Mixed) Soluble in Water, Compounds (Mixed) Soluble in Acids, Compounds Mixed) Insoluble, Particular Analytic Processes.—II., **Temperature:** Coal, Steam Heat for Printers' Stoves.—III., **Acids and Alkalies:** Boracic Acid, Muriatic Acid, Nitric Acid, Sulphuric Acid, Potash, Soda, Lithia, Calculation of Chemical Separations.—IV., **The Earths:** Alumine, Clays, Silica, Flint, Lime, Plaster of Paris, Magnesia, Barytes, Felspar, Grauen (or China Stone), China Clay, Chert.—V., **Metals:** Reciprocal Combinative Potencies of the Metals, Antimony, Arsenic, Chromium, Green Oxide, Cobalt, Chromic Acid, Humid Separation of Nickel from Cobalt, Arsenite of Cobalt, Copper, Gold, Iron, Lead, Manganese, Platinum, Silver, Tin, Zinc.

PART II., SYNTHESIS AND COMPOUNDS.—Chapters I., Sketch of the Origin and Progress of the Art.—II., **Science of Mixing:** Scientific Principles of the Manufacture, Combinative Potencies of the Earths.—III., **Bodies:** Porcelain—Hard, Porcelain—Fritted Bodies, Porcelain—Raw Bodies, Porcelain—Soft, Fritted Bodies, Raw Bodies, Stone Bodies, Ironstone, Dry Bodies, Chemical Utensils, Fritted Jasper, Fritted Pearl, Fritted Drab, Raw Chemical Utensils, Raw Stone, Raw Jasper, Raw Pearl, Raw Mortar, Raw Drab, Raw Brown, Raw Fawn, Raw Cane, Raw Red Porous, Raw Egyptian, Earthenware, Queen's Ware, Cream Colour, Blue and Fancy Printed, Dipped and Mocha, Chalky, Rings, Stilts, etc.—IV., **Glazes:** Porcelain—Hard Fritted, Porcelain—Soft Fritted, Porcelain—Soft Raw, Cream Colour Porcelain, Blue Printed Porcelain, Fritted Glazes, Analysis of Fritt, Analysis of Glaze, Coloured Glazes, Dips, Smears and Washes; **Glasses:** Flint Glass, Coloured Glasses, Artificial Garnet, Artificial Emerald, Artificial Amethyst, Artificial Sapphire, Artificial Opal, Plate Glass, Crown Glass, Broad Glass, Bottle Glass, Phosphoric Glass, British Steel Glass, Glass-Staining and Painting, Engraving on Glass, Dr. Faraday's Experiments.—V., **Colours:** Colour Making, Fluxes or Solvents, Components of the Colours; **Reds, etc., from Gold,** Carmine or Rose Colour, Purple, Reds, etc., from Iron, Blues, Yellows, Greens, Blacks, White, Silver for Burnishing, Gold for Burnishing, Printer's Oil, Lustres.

PART III., TABLES OF THE CHARACTERISTICS OF CHEMICAL SUBSTANCES.—Preliminary Remarks, Oxygen (Tables), Sulphur and its Compounds, Nitrogen ditto, Chlorine ditto, Bromine ditto, Iodine ditto, Fluorine ditto, Phosphorous ditto, Boron ditto, Carbon ditto, Hydrogen ditto, Observations, Ammonium and its Compounds (Tables), Thorium ditto, Zirconium ditto, Aluminium ditto, Yttrium ditto, Glucinum ditto, Magnesium ditto, Calcium ditto, Strontium ditto, Barium ditto, Lithium ditto, Sodium and its Compounds Potassium ditto, Observations, Selenium and its Compounds (Tables), Arsenic ditto, Chromium ditto, Vanadium ditto, Molybdenum ditto, Tungsten ditto, Antimony ditto, Tellurium ditto, Tantalum ditto, Titanium ditto, Silicium ditto, Osmium ditto, Gold ditto, Iridium ditto, Rhodium ditto, Platinum ditto, Palladium ditto, Mercury ditto, Silver ditto, Copper ditto, Uranium ditto, Bismuth and its Compounds, Tin ditto, Lead ditto, Cerium ditto, Cobalt ditto, Nickel ditto, Iron ditto, Cadmium ditto, Zinc ditto, Manganese ditto, Observations, Isomorphous Groups, Isomeric ditto, Metameric ditto, Polymeric ditto, Index.

Press Opinions.

"This interesting volume has been kept from the pencil of the modern editor and reprinted in its entirety by the enterprising publishers of *The Pottery Gazette* and other trade journals. . . . There is an excellent historical sketch of the origin and progress of the art of pottery which shows the intimate knowledge of classical as well as (the then) modern scientific literature possessed by the late Dr. Shaw; even the etymology of many of the Staffordshire place-names is given."—*Glasgow Herald.*

"The historical sketch of the origin and progress of pottery is very interesting and instructive. The science of mixing is a problem of great importance, and the query how the natural products, alumina and silica can be compounded to form the best wares may be solved by the aid of chemistry instead of by guesses, as was formerly the case. This portion of the book may be most suggestive to the manufacturer, as also the chapters devoted to the subject of glazes, glasses and colours."—*Birmingham Post.*

"Messrs. Scott, Greenwood & Co. are doing their best to place before the pottery trades some really good books, likely to aid the Staffordshire manufacturers, and their spirited enterprise is worthy of encouragement, for the utility of technical literature bearing upon the practical side of potting goes without saying. . . . They are to be congratulated on their enterprise in republishing it, and we can only hope that they will meet with the support they deserve. It seems to be a volume that is worth looking through by both manufacturers and operatives alike, and all local institutions, at any rate, should secure copies."—*Staffordshire Sentinel.*

Paper Making.

THE DYEING OF PAPER PULP. A Practical Treatise for the use of Papermakers, Paperstainers, Students and others. By JULIUS ERFURT, Manager of a Paper Mill. Translated into English and Edited with Additions by JULIUS HÜBNER, F.C.S., Lecturer on Papermaking at the Manchester Municipal Technical School. With Illustrations and **157 patterns of paper dyed in the pulp.** Royal 8vo, 180 pp. 1901. Price 15s.; India and Colonies, 16s.; Other Countries, 20s.; strictly net. Limited edition.

Contents.

I., **Behaviour of the Paper Fibres during the Process of Dyeing, Theory of the Mordant**—Cotton; Flax and Hemp; Esparto; Jute; Straw Cellulose; Chemical and Mechanical Wood Pulp; Mixed Fibres; Theory of Dyeing.—II., **Colour Fixing Mediums (Mordants)**—Alum; Aluminium Sulphate; Aluminium Acetate; Tin Crystals (Stannous Chloride); Copperas (Ferrous Sulphate); Nitrate of Iron (Ferric Sulphate); Pyrolignite of Iron (Acetate of Iron); Action of Tannic Acid; Importance of Materials containing Tannin; Treatment with Tannic Acid of Paper Pulp intended for dyeing; Blue Stone (Copper Sulphate); Potassium Bichromate; Sodium Bichromate; Chalk (Calcium Carbonate); Soda Crystals (Sodium Carbonate); Antimony Potassium Tartrate (Tartar Emetic).—III., **Influence of the Quality of the Water Used.**—IV., **Inorganic Colours**—1. Artificial Mineral Colours: Iron Buff; Manganese Bronze; Chrome Yellow (Chromate of Lead); Chrome Orange (Basic Chromate of Lead); Red Lead; Chrome Green; Blue with Yellow Prussiate; Prussian Blue; Method for Producing Prussian Blue free from Acid; Ultramarine—2. Natural Mineral Colours (Earth Colours): Yellow Earth Colours; Red Earth Colours; Brown Earth Colours; Green, Grey and Black Earth Colours; White Earth Colours; White Clay (China Clay); White Gypsum; Baryta; Magnesium Carbonate; Talc, Soapstone.—V., **Organic Colours**—1. Colours of Vegetable and Animal Origin: (*a*) *Substantive (Direct Dyeing) Colouring Matters:* Annatto; Turmeric; Safflower; (*b*) *Adjective (Indirect Dyeing) Colouring Matters:* Redwood; Cochineal; Weld; Persian Berries; Fustic Extract; Quercitron; Catechu (Cutch); Logwood Extract—2. Artificial Organic (Coal Tar) Colours: Acid Colours; Basic Colours; Substantive (Direct Dyeing) Colours; Dissolving of the Coal Tar Colours; Auramine^{OO}; Naphthol Yellow S^{O}; Quinoline Yellow^{O}; Metanil Yellow^{O}; Paper Yellow^{O}; Azoflavine RS^{O}, S^{O}; Cotton Yellow G^{xx} and R^{xx}; Orange II^{O}; Chrysoïdine A^{OO}, RL^{OO}; Vesuvine Extra^{OO}; Vesuvine BC^{OO}; Fast

Brown°, Naphthylamine Brown°; Water Blue IN°; Water Blue TB°; Victoria Blue B°°; Methylene Blue MD°°; Nile Blue R°°; New Blue S°°; Indoïne Blue BB°°; Eosine 442 Nx; Phloxine BB N; Rhodamine B°°; Rhodamine 6 G°°; Naphthylamine Red G°; Fast Red A°; Cotton Scarlet°; Erythrine RR°; Erythrine X°; Erythrine P°; Ponceau 2 R°; Fast Ponceau G° and B°; Paper Scarlet P°°; Saffranine PP°°; Magenta Powder A°°; Acetate of Magenta°°; Cerise D 10°°; Methyl Violet BB°°; Crystal Violet°°; Acid Violet 3 BN°, 4 R°; Diamond Green B°°; Nigrosine WL°; Coal Black°°; Brilliant Black B°.—VI., **Practical Application of the Coal Tar Colours according to their Properties and their Behaviour towards the Different Paper Fibres**—Coal Tar Colours, which rank foremost, as far as their fastness to light is concerned; Colour Combinations with which colourless or nearly colourless Backwater is obtained; Colours which do not bleed into White Fibres, for Blotting and Copying Paper Pulp; Colours which produce the best results on Mechanical Wood and on Unbleached Sulphite Wood; Dyeing of Cotton, Jute and Wool Half-stuff for Mottling White or Light Coloured Papers; Colours suitable for Cotton; Colours specially suitable for Jute Dyeing; Colours suitable for Wool Fibres.—VII., **Dyed Patterns on Various Pulp Mixtures**—Placard and Wrapping Papers; Black Wrapping and Cartridge Papers; Blotting Papers; Mottled and Marbled Papers made with Coloured Linen, Cotton and Union Rags, or with Cotton, Jute, Wool and Sulphite Wood Fibres, dyed specially for this purpose; Mottling with Dark Blue Linen; Mottling with Dark Blue Linen and Dark Blue Cotton; Mottling with Dark Blue Cotton; Mottling with Dark Blue and Red Cotton; Mottling with Dark Red Cotton; Mottling of Bleached Stuff, with 3 to 4 per cent. of Dyed Cotton Fibres; Mottling with Dark Blue Union (Linen and Wool or Cotton Warp with Wool Weft); Mottling with Blue Striped Red Union; Mottling of Bleached Stuff with 3 to 4 per cent. of Dyed Wool Fibres; Mottling of Bleached Stuff with 3 to 4 per cent. of Dyed Jute Fibres; Mottling of Bleached Stuff with 3 to 4 per cent. of Dyed Sulphite Wood Fibres; Wall Papers; Packing Papers.—VIII., **Dyeing to Shade**—Index.

Press Opinions.

"The book is one that is of value to every one connected with the colouring of paper."—*Paper Trade Journal.*

"The great feature of the volume is undoubtedly the series of actual patterns of dyed papers, 157 in all—twelve of which, made in England, have been added to the original German series. Detailed formulæ are given for the preparation of the pulp for each, and the tints of the samples practically form a key, by means of which the accuracy of the student's or practitioner's experiments can be tested. . . . On the whole the publication is one of distinct importance to the trade, and will no doubt speedily become a standard work of reference amongst papermakers, both in the 'lab.' and the office, as well as being an excellent text-book for the use of students in the increasing number of technical institutes in which papermaking is taught."—*World's Paper Trade Review.*

Enamelling on Metal.

ENAMELS AND ENAMELLING. An Introduction to the Preparation and Application of all Kinds of Enamels for Technical and Artistic Purposes. For Enamel Makers, Workers in Gold and Silver, and Manufacturers of Objects of Art. By PAUL RANDAU. Translated from the German. With Sixteen Illustrations. 180 pp. 1900. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

I., Introduction.—II., Composition and Properties of Glass.—III., Raw Materials for the Manufacture of Enamels.—IV., Substances Added to Produce Opacity.—V., Fluxes.—VI., Pigments.—VII., Decolorising Agents.—VIII., Testing the Raw Materials with the Blow-pipe Flame.—IX., Subsidiary Materials.—X., Preparing the Materials for Enamel Making.—XI., Mixing the Materials.—XII., The Preparation of Technical Enamels, The Enamel Mass.—XIII., Appliances for Smelting the Enamel Mass.—XIV., Smelting the Charge.—XV., Composition of Enamel Masses.—XVI., Composition of Masses for Ground Enamels.—XVII., Composition of Cover Enamels.—XVIII., Preparing the Articles for Enamelling.—XIX., Applying the Enamel.—XX., Firing the Ground Enamel.—XXI., Applying and Firing the Cover Enamel or Glaze.—XXII., Repairing Defects in Enamelled Ware.—XXIII., Enamelling Articles of Sheet Metal.—XXIV., Decorating Enamelled Ware.—XXV., Specialities in Enamelling.—XXVI., Dial-plate Enamelling.—XXVII., Enamels for Artistic Purposes, Recipes for Enamels of Various Colours.—Index.

Press Opinions.

"Should prove of great service to all who are either engaged in or interested in the art of enamelling."—*Jewellers and Watchmakers' Trade Advertiser.*

"I must inform you that this is the best book ever I have come across on enamels, and it is worth double its cost."—J. MINCHIN, Jr., Porto, Portugal, 22*nd July*, 1900.

"This is a very useful and thoroughly practical treatise, and deals with every branch of the enameller's art. The manufacture of enamels of various colours and the methods of their application are described in detail. Besides the commoner enamelling processes, some of the more important special branches of the business, such as cloisonné work are dealt with. The work is well got up, and the illustrations of apparatus are well executed. The translator is evidently a man well acquainted both with the German language and the subject-matter of the book."—*Invention.*

"This is a most welcome volume, and one for which we have long waited in this country. For years we have been teaching design applied to enamelling as well as to several other crafts, but we have not risen to the scientific side of the question. Here is a handbook dealing with the composition and making of enamels for application to metals for the most part, but also for other allied purposes. It is written in a thoroughly practical way, and its author—Paul Randau—has made its subject a very particular study. The result, like almost all things which come from the German chemical expert, is a model of good workmanship and arrangement, and no one who is in search of a handbook to enamelling, no matter whether he is a craftsman producing his beautiful translucent colours on gold, silver and copper, or the hollow-ware manufacturer making enamelled saucepans and kettles, can wish for a more useful practical manual."—*Birmingham Gazette.*

THE ART OF ENAMELLING ON METAL. By W. Norman Brown. Twenty-eight Illustrations. Crown 8vo. 60 pp. 1900. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

Chapters I., History—Cloisonné—Champs Levé—Translucent Enamel—Surface Painted Enamels.—II., Cloisonné—Champs Levés—Translucent—Painted.—III., Painted Enamel—Apparatus—Furnaces and Muffles for Firing.—IV., The Copper Base or Plate—Planishing—Cloisons—Champ Levé Plates.—V., Enamels—Trituration—Washing—Coating a Plate with Enamel—Firing Ordinary Plaques for Painting—Designing—Squaring off.—VI., Designs for Cloisonné—Designs for Painted Enamels—Technical Processes—Brushes, etc.,—Colours—Grisaille—Full-coloured Designs.

Press Opinion.

"The information conveyed in *The Art of Enamelling on Metal* is as complete as can be expected in a manual of ordinary length, and is quite ample in all respects to start students in a most interesting branch of decorative art. All necessary requisites are fully described and illustrated, and the work is one, indeed, which any one may pursue with interest, for those who are interested artistically in enamels are a numerous body."—*Hardware Metals and Machinery.*

Books on Textile and Dyeing Subjects.

THE TECHNICAL TESTING OF YARNS AND TEXTILE FABRICS. With Reference to Official Specifications. Translated from the German of Dr. J. Herzfeld. Second Edition. Sixty-nine Illustrations. 200 pp. Demy 8vo. 1901. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Yarn Testing. III., **Determining the Yarn Number.**—IV., **Testing the Length of Yarns.**—V., **Examination of the External Appearance of Yarn.**—VI., **Determining the Twist of Yarn and Twist.**—VII., **Determination of Tensile Strength and Elasticity.**—VIII., **Estimating the Percentage of Fat in Yarn.**—IX., **Determination of Moisture** (Conditioning).—**Appendix.**

Press Opinions.

"It would be well if our English manufacturers would avail themselves of this important addition to the extensive list of German publications which, by the spread of technical information, contribute in no small degree to the success, and sometimes to the supremacy, of Germany in almost every branch of textile manufacture."—*Manchester Courier.*

"This is probably the most exhaustive book published in English on the subject dealt with. . . . We have great confidence in recommending the purchase of this book by all manufacturers of textile goods of whatever kind, and are convinced that the concise and direct way in which it is written, which has been admirably conserved by the translator, renders it peculiarly adapted for the use of English readers."—*Textile Recorder.*

"A careful study of this book enables one to say with certainty that it is a standard work on the subject. Its importance is enhanced greatly by the probability that we have here, for the first time in our own language, in one volume, a full, accurate, and detailed account, by a practical expert, of the best technical methods for the testing of textile materials, whether in the raw state or in the more or less finished product."—*Glasgow Herald.*

"The author has endeavoured to collect and arrange in systematic form for the first time all the data relating to both physical and chemical tests as used throughout the whole of the textile industry, so that not only the commercial and textile chemist, who has frequently to reply to questions on these matters, but also the practical manufacturer of textiles and his subordinates, whether in spinning, weaving, dyeing, and finishing, are catered for. . . . The book is profusely illustrated, and the subjects of these illustrations are clearly described."—*Textile Manufacturer.*

DECORATIVE AND FANCY TEXTILE FABRICS.

With Designs and Illustrations. By R. T. LORD. A Valuable Book for Manufacturers and Designers of Carpets, Damask, Dress and all Textile Fabrics. 200 pp. 1898. Demy 8vo. 132 Designs and Illustrations. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., A Few Hints on Designing Ornamental Textile Fabrics.—II., A Few Hints on Designing Ornamental Textile Fabrics (continued).—III., A Few Hints on Designing Ornamental Textile Fabrics (continued).—IV., A Few Hints on Designing Ornamental Textile Fabrics (continued).—V., Hints for Ruled-paper Draughtsmen.—VI., The Jacquard Machine.—VII., Brussels and Wilton Carpets.—VIII., Tapestry Carpets.—IX., Ingrain Carpets.—X., Axminster Carpets.—XI., Damask and Tapestry Fabrics.—XII., Scarf Silks and Ribbons.—XIII., Silk Handkerchiefs.—XIV., Dress Fabrics.—XV., Mantle Cloths.—XVI., Figured Plush.—XVII., Bed Quilts.—XVIII., Calico Printing.

Press Opinions.

"The book can be strongly recommended to students and practical men."—*Textile Colourist.*

"Those engaged in the designing of dress, mantle tapestry, carpet and other ornamental textiles will find this volume a useful work of reference."—*Leeds Mercury.*

"The book is to be commended as a model manual, appearing at an opportune time, since every day is making known a growing desire for development in British industrial art."—*Dundee Advertiser.*

"Designers especially, who desire to make progress in their calling, will do well to take the hints thrown out in the first four chapters on 'Designing Ornamental Textile Fabrics'."—*Nottingham Daily Guardian.*

POWER-LOOM WEAVING AND YARN NUMBERING,

According to Various Systems, with Conversion Tables. An Auxiliary and Text-book for Pupils of Weaving Schools, as well as for Self-Instruction and for General Use by those engaged in the Weaving Industry. Translated from the German of ANTHON GRUNER. **With Twenty-six Diagrams in Colours.** 150 pp. 1900. Crown 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

I., **Power-Loom Weaving in General.** Various Systems of Looms.—II., **Mounting and Starting the Power-Loom.** English Looms.—Tappet or Treadle Looms.—Dobbies.—III., **General Remarks on the Numbering, Reeling and Packing of Yarn.—Appendix.—Useful Hints.** Calculating Warps.—Weft Calculations.—Calculations of Cost Price in Hanks.

Press Opinions.

"A long-felt want in the weaving industry has been supplied by the issue of a cheap volume dealing with the subject."—*Belfast Evening Telegraph.*

"The work has been clearly translated from the German and published with suitable illustrations. . . . The author has dealt very practically with the subject."—*Bradford Daily Telegraph.*

"The book, which contains a number of useful coloured diagrams, should prove invaluable to the student, and its handy form will enable it to become a companion more than some cumbrous work."—*Cotton Factory Times.*

"The book has been prepared with great care, and is most usefully illustrated. It is a capital text-book for use in the weaving schools or for self-instruction, while all engaged in the weaving industry will find its suggestions helpful."—*Northern Daily Telegraph.*

"The various systems are treated in a careful manner; also the different looms and their manufacture, as well as the whole processes of the work. Yarn numbering according to various systems, with conversion tables and numerous coloured diagrams, materially assist to a clear comprehension of the subject."—*Northern Whig.*

"The 'inside' managers of our textile mills in which the work is complex or greatly varied, and where yarns of different materials are in use, will find this work convenient for reference in case of novelty or difficulty. We may also say the same in relation to the textile student. Its description of the parts of the loom and their functions will be of use to the latter, being of the most elementary kind."—*Textile Mercury.*

"The author attempts to fill a gap in weaving literature caused by the neglect of many obscure points connected with the industry. A short review is given of the power-loom as a whole, followed by a description of the different parts of the machinery with their advantages and defects. . . . The book is severely technical, but must on that account be very valuable to the pupil who is determined to master this industrial art."—*Cheshire County News.*

"It is clear and concise, and gives just that knowledge in quality and amount which any student of the weaving industry ought to consider as a minimum necessary for his thorough comprehension of his future profession. The handiness and variety of the information comprised in Section III., dealing with the numbering and reeling of yarns employed in the various systems in different countries, struck us as particularly useful "—*North British Daily Mail.*

"This work brings before weavers who are actually engaged in the various branches of fabrics, as well as the technical student, the different parts of the general run of power-looms in such a manner that the parts of the loom and their bearing to each other can be readily understood. . . . The work should prove of much value, as it is in every sense practical, and is put before the reader in such a clear manner that it can be easily understood."—*Textile Industries.*

"The book under notice is intended as an instructor to those engaged in power-loom weaving, and, judging by its compilation, the author is a thorough master of the craft. It is not overloaded with details, and he manages to compress in a book of some 150 pages all that one can possibly wish to know about the different parts of the machinery, whether of English or foreign make, and for whatever kind of cloth required. A comprehensive summary is also included of the various yarns and methods of numbering them, as well as a few useful hints and a number of coloured diagrams for mandarin weavings. The book is printed in bold, legible type, on good paper, has a copious index, and is well and strongly bound."—*Ashton-under-Lyne Herald.*

"In dealing with the complicated parts of various classes of power-looms, the writer, who is one of the professors at the Royal Weaving School of Asch, brings to the work a thorough knowledge of the subject, and, what is of great value, he has the gift of communicating his knowledge in a way which is easily understood. The smallest details of loom-setting are entered into, and a full explanation of problems, which are a source of anxiety to many engaged in overlooking, is given. Students will find the work an admirable text-book, and all who are interested in weaving will see in it a valuable addition to the literature on this subject. . . The book is in small compass, and is crowded with valuable information."—*Bradford Observer.*

COLOUR: A HANDBOOK OF THE THEORY OF COLOUR.

By GEORGE H. HURST, F.C.S. **With Ten Coloured Plates** and Seventy-two Illustrations. 160 pp. Demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., **Colour and Its Production.** Light, Colour, Dispersion of White Light Methods of Producing the Spectrum, Glass Prism and Diffraction Grating Spectroscopes, The Spectrum, Wave Motion of Light, Recomposition of White Light, Hue, Luminosity, Purity of Colours, The Polariscope, Phosphorescence, Fluorescence, Interference.—II., **Cause of Colour in Coloured Bodies.** Transmitted Colours, Absorption Spectra of Colouring Matters.—III., **Colour Phenomena and Theories.** Mixing Colours, White Light from Coloured Lights, Effect of Coloured Light on Colours, Complementary Colours, Young-Helmholtz Theory, Brewster Theory, Supplementary Colours, Maxwell's Theory, Colour Photography.—IV., **The Physiology of Light.** Structure of the Eye, Persistence of Vision, Subjective Colour Phenomena, Colour Blindness.—V., **Contrast.** Contrast, Simultaneous Contrast, Successive Contrast, Contrast of Tone, Contrast of Colours, Modification of Colours by Contrast, Colour Contrast in Decorative Design.—VI., **Colour in Decoration and Design.** Colour Harmonies, Colour Equivalents, Illumination and Colour, Colour and Textile Fabrics, Surface Structure and Colour.—VII., **Measurement of Colour.** Colour Patch Method, The Tintometer, Chromometer.

Press Opinions.

"This useful little book possesses considerable merit, and will be of great utility to those for whom it is primarily intended."—*Birmingham Post.*

"It will be found to be of direct service to the majority of dyers, calico printers and colour mixers, to whom we confidently recommend it."—*Chemical Trade Journal.*

"It is thoroughly practical, and gives in simple language the why and wherefore of the many colour phenomena which perplex the dyer and the colourist."—*Dyer and Calico Printer.*

"We have found the book very interesting, and can recommend it to all who wish to master the different aspects of colour theory, with a view to a practical application of the knowledge so gained."—*Chemist and Druggist.*

"Mr. Hurst's *Handbook on the Theory of Colour* will be found extremely useful, not only to the art student, but also to the craftsman, whose business it is to manipulate pigments and dyes."—*Nottingham Daily Guardian.*

TEXTILE RAW MATERIALS AND THEIR CONVERSION INTO YARNS.

(The Study of the Raw Materials and the Technology of the Spinning Process.) Text-book for Textile, Trade and Higher Technical Schools. By JULIUS ZIPSER. Translated from German by CHARLES SALTER. 302 Illustrations. 480 pp. Demy 8vo. 1901. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Raw Materials: Cotton—Wool—Flax—Hemp—Jute—Hair—Shearing Sheep—Goat Wool—Silk—Detection and Estimation of Textile Raw Materials in Yarns and Fabrics—Tests.—**The Technology of Spinning. Cotton Spinning:** Bale Breakers—Carding—Combing—Roving—Mule Frames—Yarn Testing—Humidifiers. **Flax Spinning:** Tow Spinning—String Spinning—Carded Woollen Yarn—Belt Condenser—Fine Spinning—Yarn Numbering.—**Manufacture of True Worsted Yarn:** Semi-Worsted Yarns.—**Artificial Wool or Shoddy Spinning:** Spinning Shoddy.—**Index.**

THE COLOUR PRINTING OF CARPET YARNS. A

Useful Manual for Colour Chemists and Textile Printers. By DAVID PATERSON, F.C.S. Seventeen Illustrations. 132 pp. Demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s. Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Structure and Constitution of Wool Fibre.—II., Yarn Scouring.—III., Scouring Materials.—IV., Water for Scouring.—V., Bleaching Carpet Yarns.—VI., Colour Making for Yarn Printing.—VII., Colour Printing Pastes.—VIII., Colour Recipes for Yarn Printing.—IX., Science of Colour Mixing.—X., Matching of Colours.—XI., "Hank" Printing.—XII., Printing Tapestry Carpet Yarns.—XIII., Yarn Printing.—XIV., Steaming Printed Yarns.—XV., Washing of Steamed Yarns.—XVI., Aniline Colours Suitable for Yarn Printing.—XVII., Glossary of Dyes and Dye-wares used in Wood Yarn Printing.—Appendix.

Press Opinions.

"The book is worthy the attention of the trade."—*Worcester Herald.*

"The treatise is arranged with great care, and follows the processes described in a manner at once clear and convincing."—*Glasgow Record.*

"A most useful manual dealing in an intelligible and interesting manner with the colour printing of carpet yarns."—*Kidderminster Times.*

"An eminent expert himself, the author has evidently strained every effort in order to make his work the standard guide of its class."—*Leicester Post.*

"The book, which is admirably printed and illustrated, should fulfil the need of a practical guide in the colour printing of carpet yarns.—*Nottingham Express.*

"The subject is very exhaustively treated in all its branches. . . . The work, which is very well illustrated with designs, machines, and wool fibres, will be a useful addition to our textile literature."—*Northern Whig.*

"It gives an account of its subject which is both valuable and instructive in itself, and likely to be all the more welcome because books dealing with textile fabrics usually have little or nothing to say about this way of decorating them."—*Scotsman.*

"The work shows a thorough grasp of the leading characteristics as well as the minutæ of the industry, and gives a lucid description of its chief departments. . . . As a text-book in technical schools where this branch of industrial education is taught, the book is valuable, or it may be perused with pleasure as well as profit by any one having an interest in textile industries."—*Dundee Courier.*

"The book bears every mark of an extensive practical knowledge of the subject in all its bearings, and supplies a real want in technical literature. Chapters IX. and X., on the science of colour mixing and colour matching respectively, are especially good, and we do not remember to have seen the bearing of various kinds of light, and of the changes from one kind of light to another on the work of the colourist, so well treated elsewhere."—*Dyer and Calico Printer.*

"It is thoroughly practical, and contains much information which has not hitherto appeared in book form. It is pleasing to note that the practical part is not crowded out with purely 'practical recipes'. A few typical examples are given, and the rest is left to the common sense and judgment of the printer or works' chemist. Another pleasing feature is the accounts given here and there of the author's own researches on the subject. The work will be of interest to printers of wool generally, and to those engaged in the dyeing of this fibre."—*Journal of the Society of Dyers and Colourists.*

A PRACTICAL TREATISE ON THE BLEACHING OF LINEN AND COTTON YARN AND FABRICS. By

L. TAILFER, Chemical and Mechanical Engineer. Translated from the French by JOHN GEDDES McINTOSH, Lecturer on Chemical Technology, London. Demy 8vo. 1901. Price 12s. 6d.; India and Colonies, 13s. 6d; Other Countries, 15s.; strictly net.

Contents.

Chapter I. General Considerations on Bleaching. Chapter II. Steeping. Chapter III Washing: Its End and Importance—Roller Washing Machines—Wash Wheel (Dash Wheel)—Stocks or Wash Mill—Squeezing. Chapter IV. Lye Boiling—Lye Boiling with Milk of Lime—Lye Boiling with Soda Lyes—Description of Lye Boiling Keirs—Operations of Lye Boiling—Concentration of Lyes. Chapter V. Mather and Platt's Keir—Description of the Keir—Saturation of the Fabrics—Alkali used in Lye Boiling—Examples of Processes. Chapter VI. Soap—Action of Soap in Bleaching—Quality and Quantity of Soaps to use in the Lye—Soap Lyes or Scalds—Soap Scouring Stocks. Chapter VII. Bleaching on Grass or on the Bleaching Green or Lawn. Chapter VIII. Chemicking—Remarks on Chlorides and their Decolourising Action—Chemicking Cisterns—Chemicking—Strengths, etc. Chapter IX. Sours—Properties of the Acids—Effects Produced by Acids—Souring Cisterns. Chapter X. Drying—Drying by Steam—Drying by Hot Air—Drying by Air. Chapter XI. Damages to Fabrics in Bleaching—Yarn Mildew—Fermentation—Iron Rust Spots—Spots from Contact with Wood—Spots incurred on the Bleaching Green—Damages arising from the Machines. Chapter XII. Examples of Methods used in Bleaching—Linen—Cotton. Chapter XIII. The Valuation of Caustic and Carbonated Alkali (Soda) and General Information Regarding these Bodies—Object of Alkalimetry—Titration of Carbonate of Soda—Comparative Table of Different Degrees of Alkalimetrical Strength—Five Problems relative to Carbonate of Soda—Caustic Soda, its Properties and Uses—Mixtures of Carbonated and Caustic Alkali—Note on a Process of Manufacturing Caustic Soda and Mixtures of Caustic and Carbonated Alkali (Soda). Chapter XIV. Chlorometry—Titration—Wagner's Chlorometric Method—Prepara-

tion of Standard Solutions—Apparatus for Chlorine Valuation—Alkali in Excess in Decolourising Chlorides. Chapter XV. Chlorine and Decolourising Chlorides—Synopsis—Chlorine—Chloride of Lime—Hypochlorite of Soda—Brochoki's Chlorozone—Various Decolourising Hypochlorites—Comparison of Chloride of Lime and Hypochlorite of Soda. Chapter XVI. Water—Qualities of Water—Hardness—Dervaux's Purifier—Testing the Purified Water—Different Plant for Purification—Filters. Chapter XVII. Bleaching of Yarn—Weight of Yarn—Lye Boiling—Chemicking—Washing—Bleaching of Cotton Yarn. Chapter XVIII. The Installation of a Bleach Works—Water Supply—Steam Boilers—Steam Distribution Pipes—Engines—Keirs—Washing Machines—Stocks—Wash Wheels—Chemicking and Souring Cisterns—Various—Buildings. Chapter XIX. Addenda—Energy of Decolourising Chlorides and Bleaching by Electricity and Ozone—Energy of Decolourising Chlorides—Chlorides—Production of Chlorine and Hypochlorites by Electrolysis—Lunge's Process for increasing the intensity of the Bleaching Power of Chloride of Lime—Trilfer's Process for Removing the Excess of Lime or Soda from Decolourising Chlorides—Bleaching by Ozone.

THE SCIENCE OF COLOUR MIXING. A Manual intended for the use of Dyers, Calico Printers and Colour Chemists. By DAVID PATERSON, F.C.S. Forty-one Illustrations, **Five Coloured Plates, and Four Plates showing Eleven Dyed Specimens of Fabrics.** 132 pp. Demy 8vo. 1900. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Colour a Sensation; Colours of Illuminated Bodies; Colours of Opaque and Transparent Bodies; Surface Colour.—II., Analysis of Light; Spectrum; Homogeneous Colours; Ready Method of Obtaining a Spectrum.—III., Examination of Solar Spectrum; The Spectroscope and Its Construction; Colourists' Use of the Spectroscope.—IV.. Colour by Absorption; Solutions and Dyed Fabrics; Dichroic Coloured Fabrics in Gaslight.—V., Colour Primaries of the Scientist *versus* the Dyer and Artist; Colour Mixing by Rotation and Lye Dyeing; Hue, Purity, Brightness; Tints; Shades, Scales, Tones, Sad and Sombre Colours.—VI., Colour Mixing; Pure and Impure Greens, Orange and Violets; Large Variety of Shades from few Colours; Consideration of the Practical Primaries: Red, Yellow and Blue.—VII., Secondary Colours; Nomenclature of Violet and Purple Group; Tints and Shades of Violet; Changes in Artificial Light.—VIII., Tertiary Shades; Broken Hues; Absorption Spectra of Tertiary Shades.—Appendix: Four Plates with Dyed Specimens Illustrating Text.—Index.

Press Opinions.

"The work has evidently been prepared with great care, and, as far as we can judge, should be very useful to the dyer and colourist."—*Halifax Courier.*

"The volume, which is clearly and popularly written, should prove of the utmost service to all who are concerned with the practical use of colours, whether as dyers or painters."—*Scotsman.*

"To the practical colourist, and also to technical students, Mr. Paterson's new work will be very welcome We are often asked to recommend books on different subjects, and have no hesitation in advising the purchase of the present volume by dyers and calico printers, as containing a mass of most useful information at a nominal price."—*Irish Textile Journal.*

"Mr. Paterson's work not only clearly deals with the theory of colour, but supplies lucid directions for the practical application of the theory. His work will be found exceedingly helpful, not only to the practical colourist, but also to students in our textile colleges, by forming a useful complement to their class lectures. There are several exquisitely coloured plates and a large number of other illustrations of theory and practice in colour blending, and also a series of plates with specimens of dyed fabrics attached, in explication of the author's views."—*Wakefield Express.*

"Mr. Paterson has little to say upon the experimental aspect or on its æsthetics, but much upon the theory of colour, especially as it bears upon the question—an all-important one to dyers, calico printers and artists, who have to produce such a variety of shades and tints—of the admixture of one colour upon another. . . . The author is a dyer, and in his concluding chapters keeps well before him the special wants and requirements of dyers. He writes pleasantly and lucidly, and there is no difficulty in following him, although here and there a lapse into ambiguousness occurs. The book is well printed, generously supplied with coloured plates, very nicely if not brightly got up; and the dyed patterns at the end enhance the value of the book to the dyer."—*Textile Mercury.*

"For some time the proprietors of *The Oil and Colourman's Journal* have been engaged in the publication of a series of practical handbooks intended for the use of those interested in certain branches of technology, and the present volume is the latest addition to their list. The feature which the works have in common—and it is an all-important one in treatises of this sort—is their eminently practical character. The primary aim of the publishers is to provide scientific text-books which will be helpful to those who are either actively engaged in the practice of the arts in question, or who are studying with that immediate end in view. . . . Mr. Paterson speaks with that assured knowledge of an expert, and in the present volume, as in that which he has already contributed to the same series, he sets forth the true foundation of the art of colouring in a manner at once comprehensive and judicious. . . . For dyers, calico printers and colourists in general, whose desire it is to work with accuracy in their respective branches, the treatise will prove an invaluable guide-book, provided the principles and methods it describes are studied with intelligence and care. To this end, every encouragement has been given that well-chosen examples, carefully executed plates and diagrams, and an exhaustive index can supply."—*Glasgow Herald.*

COLOUR MATCHING ON TEXTILES.

A Manual intended for the use of Students of Colour Chemistry, Dyeing and Textile Printing. By DAVID PATERSON, F.C.S. Coloured Frontispiece. Twenty-nine Illustrations and Fourteen Specimens of Dyed Fabrics Illustrating Text. Demy 8vo. 132 pp. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Colour Vision and Structure of the Eye—Perception of Colour—Primary and Complementary Colour Sensations.—II., Daylight for Colour Matching—Selection of a Good Pure Light—Diffused Daylight, Direct Sunlight, Blue Skylight, Variability of Daylight, etc., etc.—III., Matching of Hues—Purity and Luminosity of Colours—Matching Bright Hues—Aid of Tinted Films—Matching Difficulties Arising from Contrast.—IV., Examination of Colours by Reflected and Transmitted Lights—Effect of Lustre and Transparency of Fibres in Colour Matching.—V., Matching of Colours on Velvet Pile—Optical Properties of Dyestuffs, Dichroism, Fluorescence.—VI., Use of Tinted Mediums—Orange Film—Defects of the Eye—Yellowing of the Lens—Colour Blindness, etc.—VII., Matching of Dyed Silk Trimmings and Linings and Bindings—Its Difficulties—Behaviour of Shades in Artificial Light—Colour Matching of Old Fabrics, etc.—VIII., Examination of Dyed Colours under the Artificial Lights—Electric Arc, Magnesium and Dufton, Gardner Lights, Welsbach, Acetylene, etc.—Testing Qualities of an Illuminant.—IX., Influence of the Absorption Spectrum in Changes of Hue under the Artificial Lights—Study of the Causes of Abnormal Modifications of Hue, etc.

Reissue of

THE ART OF DYEING WOOL, SILK AND COTTON.

Translated from the French of M. HELLOT, M. MACQUER and M. LE PILEUR D'APLIGNY. First Published in English in 1789. Six Plates. Demy 8vo. 446 pp. 1901. Price 5s.; India and Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Part I., **The Art of Dyeing Wool and Woollen Cloth, Stuffs, Yarn, Worsted, etc.:** Introduction.—Chapters I., Of the Vessels and Utensils used in Dyeing.—II., Of the Fixed and Fugitive, commonly called Great and Little Dye.—III., Of Colours in Grain. **Dyeing Wool:** IV., Of Blue.—V., Of the Pastel Vat—Directions for the Proper Management of the Vat—Indications when the Vat has Suffered by too much or too little Lime, the two extremes which ought carefully to be avoided—The Preparations of Indigo for the Pastel Vat.—VI., Of the Woad Vat.—VII., Of the Indigo Vat.—VIII., Of the Cold Indigo Vat with Urine—A Hot Indigo Vat with Urine—To Reheat a Urine Vat.—IX., A Cold Indigo Vat without Urine.—X., Of the Method of Dyeing Blue.—XI., Of Red.—XII., Of Scarlet in Grain, or Venetian Scarlet.—XIII., Of Fire Scarlet.—XIV., Of Crimson.—XV., Of Gum Lac Scarlet.—XVI., Of the *Coccus polonicus*, a Colouring Insect.—XVII., Of Madder Red.—XVIII., Of Yellow.—XIX., Of Brown or Fawn Colour.—XX., Of Black.—XXI., Of the Colours obtained from a Mixture of Blue and Red.—XXII., Of the Mixture of Blue and Yellow.—XXIII., Of the Mixture of Blue and Fawn Colour.—XXIV., Of the Mixture of Blue and Black.—XXV., Of the Mixture of Red and Yellow.—XXVI., Of the Mixture of Red and Fawn.—XXVII., Of the Mixture of Red and Black.—XXVIII., Of the Mixture of Yellow and Fawn Colours.—XXIX., Of the Mixture of Yellow and Black.—XXX., Of the Mixture of Fawn Colour and Black.—XXXI., Of the Principal Mixtures of the Primitive Colours by Three and Three.—XXXII., The Method of Blending Wool of Different Colours for mixed Cloth or Stuffs.—XXXIII., The Method of Preparing Felts for Trial.—XXXIV., The Method of Dyeing Woollens False Colours.—XXXV., Of Flock or Goats' Hair.—XXXVI., Of Archil, and the Method of Using It.—XXXVII., Of Logwood.—XXXVIII., Of Brazil Wood.—XXXIX., Of Fustic.—XL., Roucou.—XLI., Of French Berries.—XLII., Of Turmeric.—XLIII., Instructions for the Proof Liquor for Wool and Woollen Stuffs.

Part II., **The Art of Dyeing Silk:** Ungumming and Boiling for White.—For Boiling of Silks Intended to be Dyed.—Observations on Ungumming and Boiling.—Of White.—Of Whitening.—Sulphuring.—Observations on Whitening and Sulphuring.—Of Aluming.—Remarks on Aluming.—Of Blue.—Remarks on the Blue of Indigo.—Of Yellow.—Remarks on Yellow.—Aurora, Orange, Mordore, Gold Colour and Chamois.—Red and Crimson.—Remarks on Crimson.—Of False Crimson or the Red of Brazil.—Remarks on the Red, or Crimson of Brazil Wood.—Of Scarlet, Orange, Red and Cherry Colour.—Preparation of the Carthamus or Bastard Saffron.—Remarks on the Dye of Carthamus or Bastard Saffron.—Of the False Poppy or Fire Colour Produced with Brazil Wood.—False Rose Colour.—Of Green.—Remarks.—Of Olives.—Remarks.—Of Violet.—Of Fine Violet, or Violet in Grain.—Of False or Common Violets or Lilac.—Of the Violet of Logwood.—Remarks.—Violet of Logwood and Verdigris.—Violets of Brazil and Logwood.—Remarks.—Violets from Brazil Wood and Archil.—Of Purple, Gillyflower, and of Fine Cochineal or Purple.—Of False Purple.—Of Maroons, Cinnamons and White Lees.—Remarks.—Of Nut Greys, Thorn Greys, Black and Iron Greys and others of the same Species.—Of Black.—Softening of Black.—Black in the Raw.—Remarks on Black.—Particular Process Communicated by M. Hellot.—Genoa Crimson, a Process Proved in May, 1743.—Violet Crimson of Italy.—Half Violet.—Genoa Black for Velvets.

Part III., **The Art of Dyeing Cotton and Linen Thread, together with the Method of Stamping Silks, Cottons, etc.:** Of Dyeing in General.—Inquiry concerning Wool, Silk, Cotton and Flax.—Of Wool.—Of Silk.—Of Cotton.—Of Flax.—Conclusion from the Examina-

tion of Substances Commonly Dyed.—Of Bleaching.—Preparation for Stuffs to be Dyed.—Astringents.—Theory of Dyeing Stuffs Prepared with Alum.—Of Colouring Substances.—Of Cochineal and Colouring Insects.—Of Madder.—Of Vegetables Furnishing a Yellow Dye.—Of the Colouring Drugs Used in Dyeing without Astringents.—Of Indigo.—Of Substances Used in Dyeing Fawn and Root Colour.—Of Carthamus, Roucou, etc.—Of Black. **Of Dyeing of Cotton Thread:** Of Cleansing.—Of the Colours Employed for the Dyeing of Cotton Thread.—Of Blue.—Of Red.—Adrianople Red.—Observations on this Dye.—Of Yellow.—Of Green.—Of Violet.—Of Red Cinnamon.—Of Black.—Black for Linen and Cotton Thread by a Combination of Colours.—Of Grey.—Of More Durable Greys.—Of Musk Colour.—Olive and Duck Greens.—Of Browns, Maroons, Coffee Colours, etc.—Of Silk Stuffs Dyed of Several Colours.—The Manner of Stamping Silk, etc., in Europe.—Of a Linen with a Blue Ground and White Pattern.—Of Saxon Blue.—Observations on this Dye.—**Indexes.**

THE DYEING OF COTTON FABRICS: A Practical Handbook for the Dyer and Student. By FRANKLIN BEECH, Practical Colourist and Chemist. 272 pp. Forty-four Illustrations of Bleaching and Dyeing Machinery. Demy 8vo. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Structure and Chemistry of the Cotton Fibre.—II., Scouring and Bleaching of Cotton.—III., Dyeing Machinery and Dyeing Manipulations.—IV., Principals and Practice of Cotton Dyeing—1, Direct Dyeing; 2, Direct Dyeing followed by Fixation with Metallic Salts; 3, Direct Dyeing followed by Fixation with Developers; 4, Direct Dyeing followed by Fixation with Couplers; 5, Dyeing on Tannic Mordant; 6, Dyeing on Metallic Mordant; 7, Production of Colour Direct upon Cotton Fibres; 8, Dyeing Cotton by Impregnation with Dye-stuff Solution.—V., Dyeing Union (Mixed Cotton and Wool) Fabrics.—VI., Dyeing Half Silk (Cotton-Silk, Satin) Fabrics.—VII., Operations following Dyeing—Washing, Soaping, Drying.—VIII., Testing of the Colour of Dyed Fabrics.—IX., Experimental Dyeing and Comparative Dye Testing.—Index.

The book contains numerous recipes for the production on Cotton Fabrics of all kinds of a great range of colours, thus making it of great service in the Dyehouse, while to the Student it is of value in that the scientific principles which underlie the operations of dyeing are clearly laid down.

COTTON SPINNING (First Year). By THOMAS THORNLEY, Spinning Master, Bolton Technical School. 160 pp. 84 Illustrations. Crown 8vo. 1901. Price 3s.; Abroad, 3s. 6d.; strictly net.

Contents.

Syllabus and Examination Papers of the City and Guilds of London Institute.—Chapters I., Cultivation, Classification, Ginning, Baling and Mixing of the Raw Cotton.—II., Bale-Breakers, Mixing Lattices and Hopper Feeders.—III., Opening and Scutching.—IV., Carding.—Index to Illustrations.—General Index.

COTTON SPINNING (Intermediate, or Second Year). By THOMAS THORNLEY. 180 pp. 70 Illustrations. Crown 8vo. 1901. Price 5s.; India and British Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Syllabuses and Examination Papers of the City and Guilds of London Institute.—Chapters I., The Combing Process.—II., The Drawing Frame.—III., Bobbin and Fly Frames.—IV., Mule Spinning.—V., Ring Spinning.—Index to Illustrations.—General Index.

COTTON SPINNING (Honours, or Third Year). By THOMAS THORNLEY. 216 pp. 74 Illustrations. Crown 8vo. 1901. Price 5s.; India and British Colonies, 5s. 6d.; Other Countries, 6s.; strictly net.

Contents.

Syllabuses and Examination Papers of the City and Guilds of London Institute.—Chapters I., Cotton.—II., The Practical Manipulation of Cotton Spinning Machinery.—III., Doubling and Winding.—IV., Reeling.—V., Warping.—VI., Production and Costs.—VII., Main Driving.—VIII., Arrangement of Machinery and Mill Planning.—IX., Waste and Waste Spinning.—Index to Illustrations.—General Index.

Books for Mining Engineers and Steam Users.

RECOVERY WORK AFTER PIT FIRES. A Description of the Principal Methods Pursued, especially in Fiery Mines, and of the Various Appliances Employed, such as Respiratory and Rescue Apparatus, Dams, etc. By ROBERT LAMPRECHT, Mining Engineer and

Manager. Translated from the German. Illustrated by Six large Plates, containing Seventy-six Illustrations. 175 pp., demy 8vo. 1901. Price 10s. 6d.; India and Colonies, 11s.; Other Countries, 12s.; strictly net.

Contents.

Preface.—I., **Causes of Pit Fires:** 1, Fires Resulting from the Spontaneous Ignition of Coal; 2, Fires Caused by Burning Timber; 3, Fires Caused by Fire-damp Explosions.—II., **Preventive Regulations:** 1, The Outbreak and Rapid Extension of a Shaft Fire can be most reliably prevented by Employing little or no Combustible Material in the Construction of the Shaft; 2, Precautions for Rapidly Localising an Outbreak of Fire in the Shaft; 3, Precautions to be Adopted in case those under 1 and 2 Fail or Prove Inefficient Precautions against Spontaneous Ignition of Coal. Precautions for Preventing Explosions of Fire-damp and Coal Dust. Employment of Electricity in Mining, particularly in Fiery Pits. Experiments on the Ignition of Fire-damp Mixtures and Clouds of Coal Dust by Electricity.—III., **Indications of an Existing or Incipient Fire.**—IV., **Appliances for Working in Irrespirable Gases:** 1, Respiratory Apparatus; 2, Apparatus with Air Supply Pipes, (*a*) The Bremen Smoke Helmet, (*b*) The Müller Smoke Helmet, (*c*) The Stolz Rescue Mask; 3, Reservoir Apparatus; 4, Oxygen Apparatus. The Schwann Respiratory Apparatus. The Fleuss Respiratory Apparatus. The Improved Walcher-Gärtner Pneumatophor, (*a*) The Single Bottle Apparatus, Instructions for Using the Pneumatophor, Taking to Pieces and Resetting the Apparatus ready for Use; (*b*) Two Bottle Apparatus (Shamrock Type). The Neupert Rescue Apparatus (The Mayer-Pilar System).—V. **Extinguishing Pit Fires:** (*a*) Chemical Means; (*b*) Extinction with Water. Dragging down the Burning Masses and Packing with Clay; (*c*) Insulating the Seat of the Fire by Dams. Dam Building. Dam Work in the Fiery Pits of Southern Hungary: (*a*) Cross-dams of Clay; (*b*) Masonry Dams, Gallery Linings. Wagner's Portable Safety Dam. Analyses of Fire Gases. Isolating the Seat of a Fire with Dams: Working in Irrespirable Gases ("Gas-diving"): 1, Air-Lock Work (Horizontal Advance) on the Mayer System as Pursued at Karwin in 1894; 2, Air-Lock Work (Horizontal Advance) by the Mauerhofer Modified System. Vertical Advance. Mayer System. Complete Isolation of the Pit. Flooding a Burning Section isolated by means of Dams. Wooden Dams: (*a*) Upright Balk Dams; (*b*) Horizontal Balk Dams; (*c*) Wedge Dams, Masonry Dams. Examples of Cylindrical and Dome-shaped Dams. Dam Doors: Flooding the Whole Pit.—VI., **Rescue Stations:** (*a*) Stations above Ground; (*b*) Underground Rescue Stations.—VII., **Spontaneous Ignition of Coal in Bulk.**—Index.

Illustrations.

Sheet I., **Respiratory and Rescue Appliances—Precautions against Fire.** Figs. 1, Smoke Helmet; 2, Müller's Smoke Helmet; 3, Low-pressure Respiration Apparatus; 4, High-pressure Respiration Apparatus; 5, The Stolz Mask for Rescue Work; 6, Precautions against Fire.—Sheet II., **Respiratory and Rescue Apparatus.** Figs. 1, Recovery Work with Müller's Smoke Helmet after a Fire; 2-8, The Fleuss Respiration Apparatus; 9, The Walcher-Gärtner Pneumatophor; 10-12, Pneumatophor (Shamrock Type).—Sheet III., **Respiratory and Rescue Apparatus—Stretchers.** Figs. 1-8, Rescue Apparatus manufactured by O. Neupert's Successor (Mayer-Pilar System); 1, Front View; 2, Section through Bag and Mask; 3, Rear View; 4, Apparatus and Mask laid out Flat (view from above); 5, Apparatus and Mask laid out Flat (view from below); 6, Locking Device for Closing Bag; 7, Apparatus Complete, Mounted for Rescue Work; 8, Improved Valve in the Respiration Tubes; 9-12, **Stretchers.** Fig. 9, Stretcher Covered with Brown Canvas; 10, Stretcher Covered with Brown Canvas, fitted with Adjustable Head-rest; 11, Folding Stretcher Covered with Brown Canvas; 12, Rupprecht's Stretcher Covered with Brown Canvas; 13, Dr. Rühlmann's Stretcher.—Sheet IV., **Dams.** Figs. 1-7, R. Wagner's Portable Safety Dam.—Sheet V., **Signalling Appliances—Dam Construction—Cable Laying.** Figs. 1-3, Signalling Appliances; 1, Small Induction Apparatus for Pit Work; 2, Bell Signal for Pit Work; 3, Pit Telephone; 4-18, **Dam Construction;** 4, 5, Upright Timber Dam; 6, 7, Timber Dam with Wooden Door; 8, 9, Dome-shaped Dams; 10, 11, Dome-shaped Dam with Iron Door; 12, 13, The Wenker and Berninghaus Locking Device for Dam Doors; 14-17, Dam Construction; 18, Damming a Gallery Lined with Iron; 19, Support for Cable.—Sheet VI., **Working with Diving Gear in Irrespirable Gases—Gallery Work.** Figs. 1-4, Air-Lock Work (Mayer System); 5-7, Air-Lock (Mauerhofer's Modification of the Mayer System); 8-11, Construction of Dams at the Pluto Shaft.—Sheet VII., **Working with Diving Gear in Irrespirable Gases (Mayer System)—Appliances in the Shaft.** Figs. 1, 2, Sections of Shaft and Air Apparatus; 3, Salzmann Reducing Valve for Reserve Air Supply; 4, 5, L. v. Bremen's Respiration Apparatus with Karwin Reserve Appliance; 6, Cross Section of the Franziska Shaft; 7, Method of Supplying Air to Main Pipe and Winding same on Drum; 8, Clamp.

Press Opinions.

"A work of this extremely valuable character deserves to be made widely known amongst colliery managers and mining engineers at home and abroad."—*Coal and Iron.*

"This book is, in a manner, unique. The literature of mining accidents is fairly extensive, but it consists largely of departmental Blue Books."—*Sheffield Daily Telegraph.*

"A concise and lucid description of the principal methods pursued, especially in fiery mines, and of the various appliances employed, such as respiratory and rescue apparatus, dams, etc."—*Staffs Advertiser.*

"The prevention of spontaneous combustion in collieries and the extinction of underground fires are duties that fall heavily on many colliery managers. They should, therefore, welcome this translation of Mr. Lamprecht's German treatise."—*Ironmonger.*

"The book under notice supplies the needed full description, drawings, and mode of using these new appliances in actual fires, and should be studied by every colliery manager, seeing that even our best managed collieries have not been free from fires, more or less disastrous to life and property."—*Colliery Manager.*

THE PREVENTION OF SMOKE. Combined with the Economical Combustion of Fuel. By W. C. POPPLEWELL, M.Sc., A.M.Inst., C.E., Consulting Engineer. 46 Illustrations. 190 pp. 1901. Demy 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Introductory.—Chapters I., Fuel and Combustion.—II., Hand Firing in Boiler Furnaces.—III., Stoking by Mechanical Means.—IV., Powdered Fuel.—V., Gaseous Fuel.—VI., Efficiency and Smoke Tests of Boilers.—VII., Some Standard Smoke Trials.—VIII., The Legal Aspect of the Smoke Question.—IX., The Best Means to be adopted for the Prevention of Smoke.—Index.

GAS AND COAL DUST FIRING. A Critical Review of the Various Appliances Patented in Germany for this purpose since 1885. By ALBERT PÜTSCH. 130 pp. Demy 8vo. 1901. Translated from the German. With 103 Illustrations. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Generators—Generators Employing Steam—Stirring and Feed Regulating Appliances—Direct Generators—Burners—Regenerators and Recuperators—Glass Smelting Furnaces—Metallurgical Furnaces—Pottery Furnace—Coal Dust Firing.—Index.

Press Opinions.

"The work is worthy of perusal by all consumers of fuel. It is exceedingly well printed and illustrated."—*Chemical Trade Journal.*

"The book will appeal with force to the manufacturer as well as to the technical student, whilst it is also of far more than average interest to the general reader."—*Halifax Guardian.*

"The importance that gas and coal dust firing have attained of recent years, and especially the great interest attaching of late to the question of coal dust firing, makes the appearance of the present volume most opportune."—*Iron and Coal Trades Review.*

"The German author has long followed the development of various systems of gas firing, and in the present treatise he discusses the merits of appliances patented since 1885. His text and the numerous illustrations indispensable to it will be found useful by all who are engaged in practical work in the same field."— *North British Daily Mail.*

Books on Plumbing, Decorating, Metal Work, etc., etc.

EXTERNAL PLUMBING WORK. A Treatise on Lead Work for Roofs. By JOHN W. HART, R.P.C. 180 Illustrations. 270 pp. Demy 8vo. 1896. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Cast Sheet Lead.—II., Milled Sheet Lead.—III., Root Cesspools.—IV., Socket Pipes.—V., Drips.—VI., Gutters.—VII., Gutters (continued).—VIII., Breaks.—IX., Circular Breaks.—X., Flats.—XI., Flats (continued).—XII., Rolls on Flats.—XIII., Roll Ends.—XIV., Roll Intersections.—XV., Seam Rolls.—XVI., Seam Rolls (continued).—XVII., Tack Fixings.—XVIII., Step Flashings.—XIX., Step Flashings (continued).—XX., Secret Gutters.—XXI., Soakers.—XXII., Hip and Valley Soakers.—XXIII., Dormer Windows.—XXIV., Dormer Windows (continued).—XXV., Dormer Tops.—XXVI., Internal Dormers.—XXVII., Skylights.—XXVIII., Hips and Ridging.—XXIX., Hips and Ridging (continued).—XXX., Fixings for Hips and Ridging.—XXXI., Ornamental Ridging.—XXXII., Ornamental Curb Rolls.—XXXIII., Curb Rolls.—XXXIV., Cornices.—XXXV., Towers and Finials.—XXXVI., Towers and Finials (continued).—XXXVII., Towers and Finials (continued).—XXXVIII., Domes.—XXXIX., Domes (continued).—XL., Ornamental Lead Work.—XLI., Rain Water Heads.—XLII., Rain Water Heads (continued).—XLIII., Rain Water Heads (continued).

Press Opinions.

"This is an eminently practical and well-illustrated volume on the management of external ead work."—*Birmingham Daily Post.*

"It is thoroughly practical, containing many valuable hints, and cannot fail to be of great benefit to those who have not had large experience."—*Sanitary Journal.*

"Works on sanitary plumbing are by no means rare, but treatises dealing with external plumbing work are sufficiently scarce to ensure for Mr. Hart's new publication a hearty reception."—*The Ironmonger.*

"With Mr. Hart's treatise in his hands the young plumber need not be afraid of tackling outside work. He would do well to study its pages at leisure, so that he may be ready for it when called upon."—*Ironmongery.*

HINTS TO PLUMBERS ON JOINT WIPING, PIPE BENDING AND LEAD BURNING.

Third Edition, Revised and Corrected. By JOHN W. HART, R.P.C. 184 Illustrations. 313 pp. Demy 8vo. 1901. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Introduction.—Chapters I., Pipe Bending.—II., Pipe Bending (continued).—III., Pipe Bending (continued).—IV., Square Pipe Bendings.—V., Half-circular Elbows.—VI., Curved Bends on Square Pipe.—VII., Bossed Bends.—VIII., Curved Plinth Bends.—IX., Rain-water Shoes on Square Pipe.—X., Curved and Angle Bends.—XI., Square Pipe Fixings.—XII., Joint-wiping.—XIII., Substitutes for Wiped Joints.—XIV., Preparing Wiped Joints.—XV., Joint Fixings.—XVI., Plumbing Irons.—XVII., Joint Fixings.—XVIII., Use of "Touch" in Soldering.—XIX., Underhand Joints.—XX., Blown and Copper Bit Joints.—XXI., Branch Joints.—XXII., Branch Joints (continued).—XXIII., Block Joints.—XXIV., Block Joints (continued).—XXV., Block Fixings.—XXVI., Astragal Joints—Pipe Fixings.—XXVII., Large Branch Joints.—XXVIII., Large Underhand Joints.—XXIX., Solders.—XXX., Autogenous Soldering or Lead Burning.—Index.

Press Opinions.

"Rich in useful diagrams as well as in hints."—*Liverpool Mercury.*

"The papers are eminently practical, and go much farther into the mysteries they describe than the title 'Hints' properly suggests."—*Scotsman.*

"The articles are apparently written by a thoroughly practical man. As a practical guide the book will doubtless be of much service."—*Glasgow Herald.*

"So far as the practical hints in this work are concerned, it will be useful to apprentices and students in technical schools, as it deals mainly with the most important or difficult branches of the plumber's craft, *viz.*, joint wiping, pipe bending and lead burning. . . . 'Hints' are the most useful things to an apprentice, and there are many in this work which are not to be found in some of the text-books."—*English Mechanic.*

"22 PRYME STREET, HULL, 24*th November*, 1894.

"Gentlemen,—Your books to hand for which accept my best thanks, also for circulars. I myself got one of J. W. Hart's books on Plumbing from your traveller, and having looked through the same I can safely recommend it as being the best book I have seen. Mr. J. W. Hart treats exhaustively upon soldering and pipe bending, which are two of the most essential branches in the plumbing trade.'

THE PRINCIPLES AND PRACTICE OF DIPPING, BURNISHING, LACQUERING AND BRONZING BRASS WARE.

By W. NORMAN BROWN. 35 pp. Crown 8vo. 1900. Price 2s.; Abroad, 2s. 6d.; strictly net.

Contents.

Chapters I., Cleansing and Dipping; Boiling up and Cleansing; Dipping.—II., Scratch-brushing and Burnishing; Polishing; Burnishing.—III., Lacquering; Tools; Lacquers.—IV., Bronzing; Black Bronzing; Florentine Red Bronzing; Green Bronzing.—Index.

Press Opinions.

"Mr. Brown is clearly a master of his craft, and has also the immense advantage of being able to convey his instructions in a manner at once clear and concise."—*Leicester Post.*

"A thoroughly practical little treatise on the subject in all its branches, and one which should be in the hands of every tradesman or amateur who has lacquering to do."—*Irish Builder.*

WORKSHOP WRINKLES for Decorators, Painters, Paperhangers and Others.

By W. N. BROWN. Crown 8vo. 128 pp. 1901. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

Parts I., Decorating.—II., Painting.—III., Paper-hanging.—IV., Miscellaneous.
Arranged in alphabetical order.

HOUSE DECORATING AND PAINTING.

By W. NORMAN BROWN. Eighty-eight Illustrations. 150 pp. Crown 8vo. 1900. Price 3s. 6d.; India and Colonies, 4s.; Other Countries, 4s. 6d.; strictly net.

Contents.

Chapters I., Tools and Appliances.—II., Colours and Their Harmony.—III., Pigments and Media.—IV., Pigments and Media.—V., Pigments and Media.—VI., Pigments and Media.—VII., Preparation of Work, etc.—VIII., Application of Ordinary Colour.—IX., Graining.—X., Graining.—XI., Graining.—XII., Gilding.—XIII., Writing and Lettering.—XIV., Sign Painting.—XV., Internal Decoration.—Index.

Press Opinion.

"The author is evidently very thoroughly at home in regard to the technical subjects he has set himself to elucidate, from the mechanical rather than the artistic point of view, although the matter of correctness of taste is by no means ignored. Mr. Brown's style is directness itself, and there is no tyro in the painting trade, however mentally ungifted, who could fail to carry away a clearer grasp of the details of the subject after going over the performance."—*Building Industries.*

A HISTORY OF DECORATIVE ART. By W. NORMAN BROWN. Thirty-nine Illustrations. 96 pp. Crown 8vo. 1900. Price 2s. 6d.; Abroad, 3s.; strictly net.

Contents.

Chapters I., Primitive and Prehistoric Art.—II., Egyptian Art.—III., Assyrian Art.—IV., The Art of Asia Minor.—V., Etruscan Art.—VI., Greek Art.—VII., Roman Art.—VIII., Byzantine Art.—IX., Lombard or Romanesque Art.—X., Gothic Art.—XI., Renaissance Art.—XII., The Victorian Period.—Index.

Press Opinion.

"In the course of a hundred pages with some forty illustrations Mr. Brown gives a very interesting and comprehensive survey of the progress and development of decorative art. It cannot, of course, be pretended that in the limited space named the subject is treated exhaustively and in full detail, but it is sufficiently complete to satisfy any ordinary reader; indeed, for general purposes, it is, perhaps, more acceptable than a more elaborate treatise."—*Midland Counties Herald.*

A HANDBOOK ON JAPANNING AND ENAMELLING FOR CYCLES, BEDSTEADS, TINWARE, ETC. By WILLIAM NORMAN BROWN. Price 2s. net. [*Ready.*

Contents.

A Few Words on Enamelling—Appliances and Apparatus—Japans or Enamels—To Test Enamel for Lead—Japanning or Enamelling Metals—Japanning Tin, such as Tea Trays, and similar Goods—Enamelling Old Work—Enamel for Cast Iron—Enamel for Copper Cooking Utensils—The Enamelling Stove—Enamelling Bedsteads, Frames and similar large pieces—Paints and Varnishes for Metallic Surfaces—Varnishes for Ironwork—Blacking for Iron—Processes for Tin Plating—Galvanising—Metal Polishes—Colours for Polished Brass—A Golden Varnish for Metal—Painting on Zinc—Carriage Varnish—Japanese Varnish and its Application.—Index.

THE PRINCIPLES OF HOT WATER SUPPLY. By JOHN W. HART, R.P.C. With 129 Illustrations. 1900. 177 pp., demy 8vo. Price 7s. 6d.; India and Colonies, 8s.; Other Countries, 8s. 6d.; strictly net.

Contents.

Chapters I., Water Circulation.—II., The Tank System.—III., Pipes and Joints.—IV., The Cylinder System.—V., Boilers for the Cylinder System.—VI., The Cylinder System.—VII., The Combined Tank and Cylinder System.—VIII., Combined Independent and Kitchen Boiler.—IX., Combined Cylinder and Tank System with Duplicate Boilers.—X., Indirect Heating and Boiler Explosions.—XI., Pipe Boilers.—XII., Safety Valves.—XIII., Safety Valves.—XIV., The American System.—XV., Heating Water by Steam.—XVI., Steam Kettles and Jets.—XVII., Heating Power of Steam.—XVIII., Covering for Hot Water Pipes.—Index.

Press Opinion.

"If all plumbers were to read this book, and if they followed the instructions given, there would, we are sure, be fewer accidents from household boiler explosions, and many lives might be saved. No doubt the majority of householders know or care little about the subject, but any one who wishes to adopt the most up-to-date system of supplying hot water throughout his house will be able to do so if he reads Mr. Hart's book and follows the instruction given. It is a work that all who have charge of domestic water supply should study. It is a practical and profitable book."—*Wigan Observer.*

Brewing and Botanical.

HOPS IN THEIR BOTANICAL, AGRICULTURAL AND TECHNICAL ASPECT, AND AS AN ARTICLE OF COMMERCE. By EMMANUEL GROSS, Professor at the Higher Agricultural College, Tetschen-Liebwerd. Translated from the German. Seventy-eight Illustrations. 1900. 340 pp. Demy 8vo. Price 12s. 6d.; India and Colonies, 13s. 6d.; Other Countries, 15s.; strictly net.

Contents.

PART I., HISTORY OF THE HOP.

PART II., THE HOP PLANT. Introductory.—The Roots.—The Stem and Leaves.—Inflorescence and Flower: Inflorescence and Flower of the Male Hop; Inflorescence and Flower of the Female Hop.—The Fruit and its Glandular Structure: The Fruit and Seed.—Propagation and Selection of the Hop.—Varieties of the Hop: (*a*) Red Hops; (*b*) Green Hops; (*c*) Pale Green Hops.—Classification according to the Period of Ripening: 1. Early August Hops; 2. Medium Early Hops; 3. Late Hops.—Injuries to Growth: Malformations; Diseases Produced by Conditions of Soil and Climate: 1. Leaves Turning Yellow, 2. Summer or Sunbrand, 3. Cones Dropping Off, 4. Honey Dew, 5. Damage from Wind, Hail and Rain; Vegetable Enemies of the Hop: Animal Enemies of the Hop.—Beneficial Insects on Hops

PART III., CULTIVATION. The Requirements of the Hop in Respect of Climate, Soil and Situation: Climate; Soil; Situation.—Selection of Variety and Cuttings.—Planting a Hop Garden: Drainage; Preparing the Ground; Marking-out for Planting; Planting; Cultivation and Cropping of the Hop Garden in the First Year.—Work to be Performed Annually in the Hop Garden: Working the Ground; Cutting; The Non-cutting System; The Proper Performance of the Operation of Cutting: I. Method of Cutting: Close Cutting, Ordinary Cutting, The Long Cut, The Topping Cut; II. Proper Season for Cutting: Autumn Cutting, Spring Cutting; Manuring; Training the Hop Plant: Poled Gardens, Frame Training; Principal Types of Frames: Pruning, Cropping, Topping, and Leaf Stripping the Hop Plant; Picking, Drying and Bagging.—Principal and Subsidiary Utilisation of Hops and Hop Gardens.—Life of a Hop Garden; Subsequent Cropping.—Cost of Production, Yield and Selling Prices.

PART IV.—Preservation and Storage.—Physical and Chemical Structure of the Hop Cone.—Judging the Value of Hops.

PART V.—Statistics of Production.—The Hop Trade.—Index.

Press Opinions.

"The subject is dealt with fully in every little detail; consequently, even the veriest tyro can take away some useful information from its pages."—*Irish Farming World.*

"Farmers are but little given to reading; but nowadays brewers have to study their trade and keep abreast of its every aspect, and as far as regards our trade, to them this book especially appeals, and will be especially useful."—*Licensed Victuallers' Gazette.*

"Like an oasis in the desert comes a volume upon the above subject, by the Professor at the Higher Agricultural College, Tetschen-Liebwerd, Germany, who has been fortunate enough to obtain an excellent translator from the German in the person of Mr. Charles Salter. The paucity of works upon the history and cultivation of hops is surprising considering the scope it gives for an interesting and useful work."—*Hereford Times.*

"We can safely say that this book deals more comprehensively and thoroughly with the subject of hops than any work previously published in this country. . . . No one interested in the hop industry can fail to extract a large amount of information from Professor Gross's pages, which, although primarily intended for Continental readers, yet bear very closely on what may be termed the cosmopolitan aspects of the science of hop production."—*South Eastern Gazette.*

"This is, in our opinion, the most scholarly and exhaustive treatise on the subject of hops, their culture and preservation, etc., that has been published, and to the hop grower especially will its information and recommendations prove valuable. Brewers, too, will find the chapter devoted to 'Judging the Value of Hops' full of useful hints, while the whole scope and tenor of the book bear testimony to the studious and careful manner in which its contents have been elaborated."—*Brewers' Journal.*

"Considering the extent to which this country draws its hop supplies from abroad, this translation of Professor Gross's volume will prove an interesting and instructive addition to the library of any brewer or brewers' chemist, the more so as the work of translation has been admirably carried out in simple and vigorous English. . . . The volume is one of a valuable series of special technical works for trades and professions the publishers are issuing, and is the first so far dealing with the brewing industry."—*Burton Mail.*

"A work upon the above subject must be welcomed if for no other reason than the dearth of books dealing with so interesting a theme, but fortunately apart from this the book will afford excellent reading to all interested in hops and their culture. Professor Gross takes one over the whole field, by commencing with the earliest history of the plant—so far back as the days of ancient Greece—and from both practical, theoretical and scientific standpoints, deals with the cultivation, classification and formation of the hop. . . . In speaking of the production of new varieties sound information is given, and should be of value to those who are always in search of improvements."—*Hereford Journal.*

"This work is, without doubt, the most thorough and extensive compilation on hops ever yet offered to the public, and for this reason should be warmly welcomed and appreciated by men interested in the subject. Although primarily written for those engaged in the industry abroad, and mainly Continental in theory and practice, it nevertheless appeals to those connected with the hop growing and brewing business in England, not only by way of a comparison, but also as an instruction. The volume is at once practical and scientific, is well got up, and teems with illustrations and statistics. In a word, it is a book that should find its way into the hands of all who are occupied in hop production and distribution at home; and it also contains valuable information and suggestions for the brewers themselves."—*Brewers' Guardian.*

Public Libraries.

BRITISH LIBRARY YEAR BOOK, 1900-1901. A Record of Library Progress and Work. 54 Illustrations. Crown 8vo, 345 pp. 1900. Edited by THOMAS GREENWOOD. Price 3s.; abroad, 3s. 6d.; strictly net.

Contents.

Notes for Library Committees. Contributed Articles: The Library Rate. Some Points in Library Planning—Mr. Burgoyne. Library Classification—Mr. Jast. Developments in Library Cataloguing—Mr. Quinn. Children and Public Libraries—Mr. Ballinger. Fire Prevention and Insurance—Mr. Davis. The Educational Work of the Library Association—Mr. Roberts. The Library Assistants' Association—Mr. Chambers. British Municipal Libraries established under the various Public Libraries or Special Acts, and those supported out of Municipal Funds

giving particulars of Establishment, Organisation, Staff, Methods and Librarians. Table showing the Rate, Income, Work and Hours of the Rate-supported Libraries. Statistical Abstracts. British non-Municipal Libraries, Endowed, Collegiate, Proprietary and others, showing date of Establishment, number of Volumes, Particulars of Administration, and Librarians. Library Associations and Kindred Societies.

Press Opinions.

"This is a handbook which tells the reader everything about public libraries, great and small, in the United Kingdom. . . . The book is decidedly one of the best arranged volumes ever published, and there is no doubt that the editor has been at great pains to obtain the latest and most accurate information from all places. County, district and parish councils, ministers of religion, and schoolmasters everywhere should make themselves acquainted with its contents. Its perusal cannot fail to serve the ends of the library movement. The illustrations, of which there is a large number, are very good."—*Western* (*Cardiff*) *Mail.*

WORKS IN PREPARATION.

PRINCIPLES OF SIDEROLOGY (The Science of Iron). Translated from the German of HANNS FREIHERR V. ZÜPTNER.

STAINED GLASS (Ancient and Modern) and **FRET LEAD GLAZING.** By E. R. SUFFLING.

TREATISE ON CLOTH FINISHING. By ROBERT BEAUMONT, of Yorkshire College, Leeds.

INDIA-RUBBER; GUTTA PERCHA.

EVAPORATION, CONDENSATION AND COOLING. Calculations of Dimensions of Apparatus. By E. HAUSBRAND. Tables. For Chemists, Chemical and Mechanical Engineers.

THE CHEMICAL TECHNOLOGY OF TEXTILE FIBRES. Spinning, Washing, Bleaching, Dyeing, Printing and Finishing. By Dr. G. VON GEORGIEVICS. [*In the Press.*

WEAVING MACHINERY. Three Vols. By HARRY NISBET.

COLOUR TERMS: THEIR PROPER USE AND MEANING. By DAVID PATERSON.

LEAD AND ITS COMPOUNDS. By THOS. LAMBERT.

COTTON COMBERS AND THE COMBING PROCESS. By THOS. THORNLEY. [*In the Press.*

TIMBER. Its Physical and Chemical Properties, Description, Distribution throughout the World, Forests, Preservation of Timber, and Applications. From the French of Paul Charpentier. 179 Illustrations. About 500 pp.

USE OF WATER IN THE INDUSTRIAL ARTS. Composition—Influences—Residual Water—Purification—Analysis. From the French of H. de la Coux. 135 Illustrations. About 500 pp.

DYERS' MATERIALS: An Introduction to the Examination, Evaluation and Application of the Most Important Substances Used in Dyeing, Printing, Bleaching and Finishing. By PAUL HEERMANN, Ph.D. Translated by ARTHUR C. WRIGHT, M.A. (Oxon.), B.Sc. (Lond.). [*In the Press.*

HANDY GUIDES TO THE CHOICE OF BOOKS.

Vol. I. **PROSE FICTION.**

Vol. II. **TECHNICAL, TRADE AND COMMERCIAL BOOKS.**

Others to follow. [*In Preparation.*

The Publishers will advise when any of the above books are ready to firms sending their addresses.

LIBRARY OF THE UNIVERSITY OF CALIFORNIA